PB87-233318

Sampling and Analytical Methods Development for Dry Deposition Monitoring

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Aug 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-233318

EPA/600/4-87/011
August 1987

SAMPLING AND ANALYTICAL METHODS DEVELOPMENT FOR DRY DEPOSITION MONITORING

by

J. E. Sickles, II,
Research Triangle Institute
Research Triangle Park, North Carolina 27709

Contract No. EPA 68-02-4079

Project Officer

R. J. Paur
Methods Development and Analysis Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/4-87/011	**2.**	**3. RECIPIENT'S ACCESSION NO.** PB87-233318/AS
4. TITLE AND SUBTITLE SAMPLING AND ANALYTICAL METHODS DEVELOPMENT FOR DRY DEPOSITION MONITORING		**5. REPORT DATE** August 1987 **6. PERFORMING ORGANIZATION CODE**
7. AUTHOR(S) Joseph E. Sickles, II William A. McClenny and Richard J. Paur		**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute, RTP, NC 27709 U. S. EPA/EMSL Research Triangle Park, NC 27711		**10. PROGRAM ELEMENT NO.** **11. CONTRACT/GRANT NO.** 68-02-4079
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Environmental Monitoring Systems Laboratory/RTP Methods Development & Analysis Division, MDB/MMS Research Triangle Park, NC 27711		**13. TYPE OF REPORT AND PERIOD COVERED** Final Dec. 1983-Mar 1987 **14. SPONSORING AGENCY CODE** EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Acid deposition is the transfer of acidic substances to the earth's surface by wet or dry deposition. Dry deposition includes all processes by which airborne contaminants are removed from the atmosphere at the earth's surface, excluding those processes directly aided by precipitation, and contributes substantially to the acidic deposition burden. The U.S. Environmental Protection Agency (EPA) plans to implement a dry deposition monitoring network. The constitutents of interest are HNO_3, NO_2, SO_2, NH_3, NH_4^+, NO_3^-, SO_4^{2-}, H^+ (acidity), and O_3. The objective of the current research is to investigate sampling and analysis methods for these constituents to identify those methods that appear most promising for network deployment.

The culmination of the current project is a field study conducted in the Research Triangle Park, North Carolina between August and December of 1986. The main objectives of this study were to conduct measurements of selected airborne gaseous and particulate acidifying species using different types of samplers and to evaluate the differences observed under field sampling conditions. The bulk of this report presents and compares results collected in the 1986 field study using the annular denuder systen (ADS) with those collected using the transition flow reactor (TFR). Comparisons are also made with results from the filter pack (FP) tunable diode laser absorption spectroscopic (TDLAS) methods and methods of other investigators.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	**19. SECURITY CLASS** *(This Report)* UNCLASSIFIED	**21. NO. OF PAGES** 230
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	**22. PRICE**

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

Although the information in this document has been funded by the U.S. Environmental Protection Agency under Contract No. EPA 68-02-4079 with the Research Triangle Institute, Research Triangle Park, North Carolina, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, has responsibility for assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency, including the EPA component of the National Acid Precipitation Assessment Program (NAPAP).

A significant portion of EPA's participation in NAPAP involves operation of the National Trends Network (NTN). The NTN is designed to monitor acidic dry deposition by use of an inferential method which involves monitoring the concentration of relevant chemical species and estimating the flux of acidic deposition from the concentrations and independent determination of the deposition velocities. The relatively long sampling periods (generally one week) and the low concentrations involved required an evaluation/development program to select the sampling and analysis methods to be used by NTN. This report describes the major activities and results of the dry deposition methods evaluation/development program.

John C. Puzak
Acting Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27711

ABSTRACT

Acid deposition is the transfer of acidic substances to the earth's surface by wet or dry deposition. Dry desposition includes all processes by which airborne contaminants are removed from the atmosphere at the earth's surface, excluding those processes directly aided by precipitation, and contributes substantially to the acidic deposition burden. The U.S. Environmental Protection Agency (EPA) plans to implement a dry deposition monitoring network. The constituents of interest are HNO_3, NO_2, SO_2, NH_3, NH_4^+, NO_3^-, SO_4^{2-}, H^+ (acidity), and O_3. The objective of the current research is to investigate sampling and analysis methods for these constituents to identify those methods that appear most promising for network deployment.

A phased approach consisting of literature reviews, laboratory studies and field evaluations was employed. Literature reviews were used to identify those methods that appeared promising for direct application or for development into methods suitable for field application. The identified methods were tested and refined in laboratory studies. In those cases where the methods remained potentially acceptable after laboratory investigation, field evaluation studies were performed.

The culmination of the current project is a field study conducted in the Research Triangle Park, North Carolina between August and December of 1986. The main objectives of this study were to conduct measurements of selected airborne gaseous and particulate acidifying species using different types of samplers and to evaluate the differences observed under field sampling conditions. The bulk of this report presents and compares results collected in the 1986 field study using the annular denuder system (ADS) with those collected using the transition flow reactor (TFR). Comparisons are also made with results

from the filter pack (FP) tunable diode laser absorption spectroscopic (TDLAS) methods and methods of other investigators. The overall goal is to use the results of the field evaluation along with other information gathered during this project to assess the current status of available sampling and analysis methods and identify method strengths and weaknesses that must be considered prior to their field deployment.

This report was submitted in fulfillment of Contract No. 68-02-4079 by the Research Triangle Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from December 13, 1983 to June 30, 1987, and work was completed as of March 31, 1987.

CONTENTS

Page

Disclaimer ii
Foreword iii
Abstract iv
Figures viii
Tables xi
Acknowledgements xiii

1. Introduction 1
    Objective 1
        Species to be Measured 2
        Time Resolution 2
        Quality of Measurements 3
        Method Complexity 3
    Approach and Accomplishments 4
    Background 7
        Chemical-Specific Methods 7
        Multiple Constituent Systems 24
2. Conclusions and Recommendations 33
3. Experimental 41
4. Results and Discussion 43
    Quality Assurance and Quality Control Activities . . . 43
        Analysis of Quality Control Solutions 43
        Replicate Analyses 43
        Laboratory Intercomparisons 45
        Blank Results 50
        Volumetric Flow Measurement 54
        Quality Control Check for TRF Nitric Acid Concentration 56
    Special Studies 57
        Nitric Acid Spiking Experiments 57
        Interaction of Nitric Acid in Cyclones 60
        Cyclone Bleed Filter 61
        Cyclone Performance 66
        Volatilized Fine Nitrate 69
        Behavior of Ammonium Nitrate 75
        H^+ and Ion Balances 76
        Collection of SO_2 on TFR Nylon Filter 77
        Nitrite on TFR Nylon Filter 78
        Conversion of Nitrite to Nitrate in ADS 78
        Comparison of ADS and TFR Results 80
        Comparison of Operational Features of TFR and ADS . . 114
        Relationships of Fine Particulate NH_4^+ and SO_4^{2-} . . . 115
References 131

CONTENTS
(continued)

Page

Appendices

A. Development of a Method for the Sampling and Analysis of SO_2 and NO_2 from Ambient Air 137
B. Laboratory Testing of Annular Denuders and Nylon Filters . 149
C. Protocol for the Annular Denuder System 155
D. PAN Interference Testing with the LMA-3 NO_2 Detector . . . 169
E. Comparison of the Absorption of HNO_3 by Two Brands of Nylon Filters 171
F. Data Summary for Fall 1986 Field Study Using ADS and TFR . 173
G. EMSL Fall 1986 Dry Deposition Methods Comparison Study--Across Methods Comparison 181

FIGURES

Number Page

1 Transition flow reactor sampling system 27

2 Annular denuder sampling system 30

3 Nitric acid transmission for the EPA style TFE cyclone 62

4 Nitric acid transmission for the FEP Teflon-coated aluminum cyclone . . . . , 63

5 Nitric acid transmission for the TFE Italian cyclone . . . 64

6 Daily mean nitrate concentrations on ADS and TFR cyclones 67

7 Daily mean sulfate concentrations on ADS and TFR cyclones 68

8 Daily mean ratio of cyclone nitrate to total gaseous and particulate nitrate on ADS and TFR 71

9 Daily mean ratio of cyclone to total particulate sulfate in ADS and TFR 72

10 Daily mean ratio of cyclone to total particulate ammonium on ADS and TFR 73

11 Mean daily Total NH_3^++NH_4^+ concentrations from ADS and TFR samplers 83

12 Mean daily Fine (particulate) NH_4^+ concentrations from ADS and TFR samplers 84

13 Mean daily NH_3 concentrations from ADS and TFR samplers. . 85

14 Mean daily hydrogen ion concentrations from the extracts of ADS and TFR Teflon filters 86

15 Mean daily Total NO_3^- concentrations from ADS and TFR samplers 87

16 Mean daily Fine (particulate) NO_3^- concentrations from ADS sampler 88

17 Mean daily NO_3^- concentrations from the extracts of ADS and TFR Teflon filters 89

FIGURES
(continued)

Number Page

18 Mean daily HNO_3 concentrations from ADS and TFR samplers 90

19 Mean daily HONO concentrations from ADS sampler 91

20 Mean daily NO_2 concentrations from TFR sampler 92

21 Mean daily Total (particulate) SO_4^{2-} concentrations from ADS and TFR samplers 93

22 Mean daily Fine (particulate) SO_4^{2-} concentrations from ADS and TFR samplers 94

23 Mean daily SO_2 concentrations from ADS and TFR samplers 95

24 Mean weekly Total NH_3+NH_4^+ concentrations from ADS sampler 96

25 Mean weekly Fine (particulate) NH_4^+ concentrations from ADS sampler 97

26 Mean weekly NH_3 concentrations from ADS sampler 98

27 Mean weekly hydrogen ion concentrations from the extracts of ADS Teflon filters 99

28 Mean daily Total NO_3^- concentrations from ADS sampler . . . 100

29 Mean weekly Fine (particulate) NO_3^- concentrations from ADS sampler 101

30 Mean weekly NO_3^- concentrations from the extracts of ADS Teflon filters 102

31 Mean weekly HNO_3 concentrations from ADS sampler 103

32 Mean weekly HONO concentrations from ADS sampler 104

33 Mean daily Total NO_3 concentrations from ADS and TFR samplers 105

FIGURES
(continued)

Number Page

34 Mean weekly Fine (particulate) SO_4^{2-} concentrations from ADS sampler 106

35 Mean weekly SO_2 concentrations from ADS sampler 107

36 Comparison of Fine (particulate) NH_4^+ and SO_4^{2-} data collected in the September 1985 Los Angeles field study using ADS sampler 121

37 Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the spring of 1986 using ADS sampler 122

38 Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the summer of 1986 using ADS sampler 123

39 Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the summer of 1986 using TFR sampler 124

40 Comparison of weekly Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the fall of 1986 using ADS sampler 125

41 Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the fall of 1986 using TFR sampler 126

42 Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the fall of 1986 using ADS sampler 127

43 Composite of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the spring, summer, and fall of 1986 using ADS sampler 130

TABLES

Number Page

1 Contributors to ecosystem acidification 1

2 Summary of separate reports and presented papers produced under the current contract 5

3 Summary of appended reports of selected studies performed under the current contract 6

4 Summary of multiple constituent sampling systems and species sampled 25

5 Status of chemical-specific sampling and analysis methods for dry deposition 34

6 Results of analysis of QC solutions 44

7 Summary of replicate analyses 44

8 Comparison of nitrogen dioxide-spiked samples 46

9 Comparison of analysis of nitrate and sulfate QA samples prepared by EPA (Ellestad) 48

10 Interlaboratory comparisons of field samples 49

11 Blank results 51

12 Summary of estimated EAC's and DL's for daily operation of the ADS and TFR samplers 52

13 Flow rates for ADS and TFR samplers during the intensive measurement period 55

14 Results of nitric acid spiking experiments 59

15 Results of nitric acid absorption and recovery tests with cyclones 65

16 Studywide averages of daily cyclone catch contributions for TFR and ADS 70

17 Mass and percent contribution of species recovered from second denuder 80

18 Summary of concentration and precision results for ADS and TFR samplers 108

TABLES
(continued)

Number — Page

19 Comparison of ADS and TFR results 110

20 Summary of reported precision (median CVs) for ADS and TFR sampler operation in several field studies 116

21 Positive and negative operational features associated with the ADS and TFR systems 117

22 Summary of suggestions by ADS and TFR operators 118

23 Summary of regression analyses of NH_4^+ and SO_4^{2-} data from four field studies 128

ACKNOWLEDGEMENTS

This project was conducted by the Research Triangle Institute (RTI) under Contract Number 68-02-4079 for the U.S. Environmental Protection Agency (EPA). The support of this organization is gratefully acknowledged as is the advice and guidance of Dr. R. J. Paur, of EPA, who served as Project Officer.

Several persons from various organizations have contributed substantially to this project. Dr. I. Allegrini, Dr. C. Perrino, Dr. A. Febo, Dr. F. DeSantis, and Dr. M. Possanzini of the Consiglio Nazionale delle Ricerche in Rome, Italy made major contributions to field studies performed in the spring and fall of 1985 by generously sharing their expertise in the operation of the annular denuder systems. Dr. R. J. Paur, Mr. R. K. Stevens, Mr. T. G. Ellestad, and Dr. W. A. McClenny of the EPA have provided advice and assistance at various stages of this effort. Dr. K. G. Anlauf and Dr. H. A. Wiebe of Environment Canada generously provided both published and unpublished information about their experiences in developing and using sampling and analysis methods for acidifying species. Mr. P. M. Grohse, Dr. E. D. Estes, Ms. K. W. Cox, Dr. M. X. Umana, Mr. D. Whitaker, Mr. K. W. Thomas, and Dr. L. S. Sheldon of RTI contributed to one or more of the literature reviews that were conducted under this contract. Analytical laboratory operations were adeptly performed at RTI by Ms. A. R. Turner, Ms. L. L. Hodson, Ms. C. K. Sokol, Ms. K. W. Cox, Dr. E. D. Estes, and Ms. E. H. Steere. Global Geochemistry of Canoga Park, CA provided analytical services during the 1985 Los Angeles field study. Ms. L. L. Hodson, Mr. E. E. Rickman, Jr., Dr. M. L. Saeger, Mr. D. L. Hardison, Ms. K. W. Cox, and Ms. C. A. Salmons made substantial contributions to laboratory and field development and testing of various sampling and analysis methods. Ms. B. F. Magram is gratefully acknowledged for her skillful preparation of the manuscript. The efforts of all these individuals are gratefully acknowledged for bringing this project to a successful conclusion.

J. E. Sickles, II
Project Leader

SECTION 1

INTRODUCTION

OBJECTIVE

The phenomenon of acid deposition has received increasing public, political, and media attention in recent years. Acid deposition is the transfer of acidic substances to the earth's surface by wet or dry deposition. Dry deposition includes all processes by which airborne contaminants are removed from the atmosphere at the earth's surface, excluding those processes directly aided by precipitation. Dry deposition contributes substantially to the acidic deposition burden, at times accounting for more than 50 percent of the total. Efforts to monitor dry deposition and to investigate its behavior will provide insight into its role in the larger problem of acidic deposition.

The U.S. Environmental Protection Agency (EPA) plans to implement a dry deposition monitoring network. The constituents of interest and the sampling and analysis methods to be used, however, require definition. Many of the airborne chemicals that are thought to be important contributors to ecosystem acidification are given in Table 1 along with their nominal concentrations.

TABLE 1. CONTRIBUTORS TO ECOSYSTEM ACIDIFICATION

Constituent		Concentration ($\mu g/m^3$)
HNO_3	nitric acid	0.1 - 10
HNO_2	nitrous acid	0.1 - 2
NO_2	nitrogen dioxide (an acidifying precursor)	0.2 - 30
SO_2	sulfur dioxide (an acidifying precursor)	0.1 - 20
NH_3	ammonia	0.1 - 30
NH_4^+	ammonium (particulate)	0.05 - 5
NO_3^-	nitrates (particulate)	0.1 - 5
SO_4^{2-}	sulfates (particulate; may be H_2SO_4, NH_4HSO_4, or $(NH_4)_2SO_4$)	0.2 - 20
H^+ and Acidity	strong hydrogen ion (particulate)	0.01 - 10
O_3	ozone (an oxidant)	2 - 200
H_2O_2	hydrogen peroxide (an oxidant)	0.1 - 5
RCOOH	organic acids	0.1 - 10
PAN	peroxyacetyl nitrate (an oxidant)	0.05 - 50
HCHO	formaldehyde	0.1 - 50

The objective of the current research is to investigate sampling and analysis methods for several of the constituents in the above list. Emphasis has been placed on the first nine species, excluding nitrous acid. The overall goal is to identify those methods that appear most promising for network deployment.

The selection of methods for the determination of acidifying species in ambient air depends on several factors. The most important of these are the goals of the program that require the measurements and operational considerations. Normally, the selection process will involve balancing the program needs and practical limitations to arrive at workable methods.

Currently, the goals of several programs require the determination of dry deposition of acidifying species. These studies include trends monitoring, and measurements to support effects assessments, modeling efforts, and research activities. The following points must be considered in selecting sampling and analysis methodologies: species to be measured, time resolution, quality of measurements, and method complexity.

Species to be Measured

The species for consideration are: HNO_3, NO_2, SO_2, NH_3, NH_4^+, NO_3^-, SO_4^{2-}, H^+ (acidity), and O_3. This listing is expected to change with increased understanding of the important species and processes that influence ecosystem acidification.

Time Resolution

Although the time resolution has not been firmly defined, the needs of large-scale air quality models will heavily influence these requirements. Currently, time resolution ranging from 6 hours to 1 week is anticipated to be sufficient to satisfy program needs. As a result, integrated sampling over the required time scale can be employed. This eliminates the requirement for complex and capital intensive continuous instrumentation in many cases.

Quality of Measurements

Accuracy and precision define the quality of measurements. Although not yet established for the current program, reasonable accuracy and precision goals for monitoring activities are ± 10 to 20 percent. It is expected that these will differ and depend on the reactivity/importance of the species under consideration. Several factors influence the quality of the measurements: collection and recovery efficiency, sensitivity, species concentration, selectivity, and susceptability to contamination.

Collection and recovery efficiencies above 80 percent are desirable. However, if such efficiencies for potential methods are lower but precise, the method may still be viable.

Sensitivity, species concentration, and sampling rate are interrelated. Since monitoring sites are expected to be located in relatively remote locations, species concentrations are expected to be quite low (i.e., ppb to ppt levels). The sensitivity of the anlytical finish wil determine the minimum amount of the species of interest that must be sampled. The air concentration of the species, along with the time resolution requirement, will define the minimum sampling flow rate. Ambient sampling rates range from 0.1 to 10^3 Lpm. Hardware constraints may limit this range to 1 to 30 Lpm.

The method must be selective. Ideally, it would be free of physical influences such as humidity and temperature effects. In addition, it should be free of chemical interferents.

Susceptibility to contamination should be identified and minimized. Opportunities for contamination arise during sample preparation, from impure reagents, improperly cleaned glassware, human contact, and storage before and after sampling.

Method Complexity

The recommended methods are expected to be used by competent but not necessarily highly skilled field technicians. The analytical finish is expected to be performed in a well equipped laboratory using established, well developed, but not prototype or research, equipment.

As a result, the methods must be simple to use in the field and should require minimal manipulation of the sample, both in the field and in the laboratory.

APPROACH AND ACCOMPLISHMENTS

A phased approach consisting of literature reviews, laboratory studies, and field evaluations has been employed. Literature reviews have been used to identify those methods that appear promising for direct application or for development into methods suitable for field application. The identified methods have been tested and refined in laboratory studies. In those cases where the methods remained potentially acceptable after laboratory investigation, field evaluation studies were performed.

Many individual tasks have been performed under the contract. Several of these efforts resulted in separate reports and presented papers: they are identified in Table 2. The results of selected tasks not reported elsewhere are summarized in the appendices. They are mainly laboratory studies and are identified in Table 3.

The ultimate focus of the current effort has been on field evaluation of sampling and analysis methods for atmospheric constituents that contribute to acidic deposition. Two major field tests were conducted in 1985 and 1986. The first took place near Los Angeles in September of 1985 (see entries 10 to 12 in Table 2). The annular denuder system (ADS) used in that study was built by an Italian research group in Rome. The ADS measurements of HNO_3 in that field trial were 40 percent low in comparison to tunable diode laser absorption spectroscopic (TDLAS) measurements. Examination of the results of that test lead to improved understanding of the importance of inlet design, alteration of the Italian filter extraction procedures, and several hardware modifications that have resulted in more reliable operation of the ADS. The second field study is the culmination of the current project and was conducted in the Research Triangle Park, North Carolina between August and December of 1986. The main objectives of this study were to conduct measurements of selected airborne gaseous and particulate

TABLE 2. SUMMARY OF SEPARATE REPORTS AND PRESENTED PAPERS PRODUCED UNDER THE CURRENT CONTRACT

---

1. Sickles, J. E., II and Grohse, P. M. Sampling and Analysis Methods for Sulfur Dioxide and Nitrogen Dioxide: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-01I, December 1984. 54 pp.

2. Estes, E. D. and Sickles, J. E., II. Sampling and Analysis Methods for Ammonia and Ammonium Ion: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-03I, May 1985. 49 pp.

3. Cox, K. W. and Sickles, J. E., II. Sampling and Analysis Methods for Nitric Acid: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-04I, May 1985. 35 pp.

4. Grohse, P. M. and Sickles, J. E., II. Sampling and Analysis Methods for Particulate Sulfate and Nitrate: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-02I, June 1985. 50 pp.

5. Estes, E. D. and Sickles, J. E., II. Sampling and Analysis Methods for pH and Acidity: A Literature Review, Research Triangle Institute Report No. RTI/2823/00-05I, July 1985. 28 pp.

6. Estes, E. D., Umana, M. X., and Sickles, J. E., II. Sampling and Analysis Methods for Ozone: First Draft of a Literature Review. Research Triangle Institute Report No. RTI/2823/00-06I, July 1985. 39 pp.

7. Thomas, K. W., Sheldon, L. S., and Sickles, J. E., II. Sampling and Analysis Methods for Organic Acids: First Draft of a Literature Review. Research Triangle Institute Report No. RTI/2823/00-07I, August 1985. 35 pp.

8. Umana, M. X., Whitaker, D., and Sickles, J. E., II. Sampling and Analysis Methods for Hydrogen Peroxide: First Draft of a Literature Review. Research Triangle Institute Report No. RTI/2823/00-09I, December 1985. 62 pp.

9. Stevens, R. K., Paur, R. J., Allegrini, I., DeSantis, F., Febo, A., Perrino, C., Possanzini, M., Cox, K. W., Estes, E. D., Turner, A. R., and Sickles, J. E., II. Measurement of HNO_3, SO_2, NH_3, and Particulate Nitrate with an Annular Denuder System in Proceedings of Fifth Annual National Symposium on Recent Advances in the Measurement of Air Pollution. May 14-16, 1985. Raleigh, NC.

10. Sickles, J. E., II, Perrino, C., Allegrini, I., Febo, A., Possanzini, M., and Paur, R. J. Performance and Results of the Annular Denuder System in the Sampling and Analysis of Ambient Air Near Los Angeles in Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants. EPA Report No. 600/9-86-013. pp. 522-533.

11. Sickles, J. E., II, Perrino, C., Allegrini, I., Febo, A., Possanzini, M., and Paur, R. J. Performance and Results of the Annular Denuder System in the Sampling and Analysis of Ambient Air Near Los Angeles. Paper with extended abstract presented at 192nd American Chemical Society Meeting. Anaheim, CA. September 7-12, 1986.

12. Hering, S. V., *et al*. (1987) The Nitric Acid Shootout: Field Comparison of Measurement Methods. Submitted to *Atmos*. *Environ*.

TABLE 3. SUMMARY OF APPENDED REPORTS OF SELECTED STUDIES PERFORMED UNDER THE CURRENT CONTRACT

Appendix	Report Title
A	Development of a Method for the Sampling and Analysis of SO_2 and NO_2 from Ambient Air
B	Laboratory Testing of Annular Denuders and Nylon Filters
C	Protocol for the Annular Denuder System
D	PAN Interference Testing with the LMA-3 NO_2 Detector
E	Comparison of the Absorption of HNO_3 by Two Brands of Nylon Filters
F	Data Summary for Fall 1986 Field Study Using ADS and TFR
G	EMSL Fall 1986 Dry Deposition Methods Comparison Study--Across Methods Comparison

acidifying species using different types of samplers and to evaluate the differences observed under field sampling conditions. The bulk of this final report presents and compares results collected in the 1986 field study using the ADS with those collected using the transition flow reactor (TFR).

Comparisons are also made in Appendix G with results from the filter pack (FP), TDLAS methods, and methods of other investigators involved in the Fall 1986 Field Evaluation Study. The overall goal is to use the results of the field evaluation along with other information gathered during this project to assess the current status of available methods and identify method strengths and weaknesses that must be considered prior to their field deployment.

BACKGROUND

Two broad types of methods are available for sampling acidifying dry deposition constituents: chemical-specific methods and multiple-constituent systems. Descriptions of these methods are given in the following sections. The information presented here summarizes literature findings and experimental results obtained as of July 1986. As a result, it provides a good background for the analysis of the data collected in the Fall 1986 Field Evaluation Study.

Chemical-Specific Methods

Methods for each chemical species identified earlier in Table 1 are described below.

HNO_3--

The interest in nitric acid has led to the development of various collection and analysis techniques, including microcoulometry, chemiluminescence (CLM), IR absorption, filtration, and denuder tubes (1).

Filter media have been used to a large extent in the determination of nitric acid. These techniques generally employ dual filters that rely on the collection of particulate nitrate on the first filter and gaseous nitric acid on the second filter. Typically, they are used in conjunction with instrumental detection or subsequent chemical analysis of the material collected on the filter media. High nitric acid collection has been found with NaCl-impregnated cellulose filters and with nylon filters (2,3).

Although the HNO_3 determination by dual-filter methods is desirable due to low cost, simplicity, and high sensitivity, there is great difficulty in distinguishing between gaseous and particulate forms of nitrate. Errors in the measurement of gaseous HNO_3 may be in the form of positive artifact due to:

- Volatilization of collected aerosol nitrates on the prefilter to form gaseous nitric acid (i.e., $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$); or
- Reaction of collected particulate nitrates on the prefilter with strong acids, resulting in the release of HNO_3 (i.e., $H_2SO_4 + 2NH_4NO_3 \rightarrow (NH_4)_2SO_4 + 2HNO_3$); or
- Formation of HNO_3 on the collection medium by interaction with NO_2, especially under humid conditions.

Negative nitric acid artifact may result from:

- Retention of HNO_3 by the prefilter collection medium; or
- Retention of HNO_3 by collected particles on the prefilter;
- A low capacity for HNO_3 on the collection medium; or
- Losses of HNO_3 by volatilization or by displacement by other acids.

Inert prefilter materials, such as Teflon, should not collect HNO_3; this, however, does not preclude the possibility of HNO_3 reaction with aerosol particles collected on Teflon. In addition, some types of Teflon (e.g., TFE) may sorb HNO_3 to a larger extent than others (e.g., FEP and PFA). This underscores the importance of using "inert" materials for all surfaces coming into contact with HNO_3 (4).

To avoid some of the artifact problems, denuder tube assemblies were introduced. The system consists of two parallel filter pack assemblies, one to measure total inorganic nitrate (TIN) and the other, preceded by a coated denuder tube, to measure particulate nitrate (PN).

The denuder removes gaseous nitric acid while permitting particles to pass when sampling under conditions of laminar flow. HNO_3 is determined either by the difference in nitrate found in these two assemblies (denuder difference experiment) or by the analysis of the denuder tube extract for nitrate (5).

Denuder tubes have been coated with MgO, Na_2CO_3, nylon, and tungstic acid for nitric acid collection. Each of these materials has specific problems. Tungstic acid tubes are difficult to prepare and have low capacity. It is claimed that Na_2CO_3 tubes require special care during sampling to prevent Na_2CO_3 dissolution under conditions of high humidity (6). It is difficult to maintain good coating adhesion in MgO tubes if frequent handling of the tube is necessary.

Nylon as a collection medium for HNO_3 has some limitations, namely collection capacity. Nylon filters have been reported to collect over 90 percent of the delivered HNO_3 up to loadings of 440 μg/47 mm filter (7). At a nominal HNO_3 concentration of 1 $\mu g/m^3$, a sampler operating at 15 Lpm can sample for 20 days without exceeding the filter capacity. However, at ambient levels of 5 $\mu g/m^3$, the capacity is exceeded in 4 days. Thus, it appears that except under heavily polluted circumstances, the collection capacity of nylon filters for HNO_3 should be adequate for one-week samples. A second limitation of nylon filters is that the fabrication process and/or quality of raw materials is variable and has changed at least twice between 1985 and 1986, resulting in different chemical and physical filter characteristics (e.g., increased capacity for SO_2 and reduced pressure drop)(8). In addition, nylon appears to be effective at collecting HNO_2 (see Appendix A). These chemical characteristics, as well as its physical properties, should be important considerations in the design of multiple constituent sampling systems.

A new type of denuder tube has recently been developed--the annular denuder (9). In the annular denuder, ambient air is passed through the annular space of two concentric tubes. The outside of the inner tube and the inside of the outer tube are coated with a specific gas-absorbing solution. For collecting nitric acid as well as nitrous acid and SO_2, this coating is Na_2CO_3. The annular design permits a reduction in denuder tube length and an increase in flow rates over the conventional open-tube denuder design.

A second recent innovation in the sampling of nitric acid is the transition flow reactor (TFR) (10). This approach uses a nylon strip as a partial denuder to remove a constant fraction of the gaseous HNO_3 under transition flow conditions. The strip is followed by a Teflon and a nylon filter. The total gaseous HNO_3 is calculated from the analysis of nitrate from the nylon strip, and the particulate is then determined algebraically, using the nitrate found on the Teflon and nylon filters.

It should be noted that the highest recoveries of HNO_3 from nylon are found with a basic extraction solution, rather than DI water (see Appendix B). Laboratory studies have shown 0.003 N NaOH to be adequate. It is recommended that extraction and analysis be performed promptly after sampling; however, when this is not feasible, extraction should be performed promptly, and the extract should be stored under refrigeration until analysis.

Suggested methods for the analysis of material collected on filter media or of denuder tube extracts are colorimetry, gas chromatography (GC), and ion chromatography (IC)(1). IC analysis requires fairly complex instrumentation but is selective, sensitive, and may be used with all filter materials considered for collecting HNO_3, except NaCl-impregnated cellulose. In this case, the Cl^- peak often obscures the NO_3^- peak.

It is recommended that a denuder-filter combination be used to sample for HNO_3. The denuder concept for sampling reactive gases, namely HNO_3, is well accepted; however, flow rate limitations are a serious drawback for routine field use of a conventional laminar flow open channel denuder. As a result, the ADS or TFR should be considered. The collected nitrate should be determined by IC.

HNO_2--

Nitrous acid is a compound of potential significance in the dry deposition of nitrogen species. Currently, relatively few methods have been examined for collection of HNO_2, and no methods have been extensively evaluated. Nitrous acid has received relatively little attention in atmospheric chemistry studies. Since HNO_2 photolyzes in sunlight to nitric oxide and the highly reactive hydroxyl radical, it has been suspected as a constituent of major importance in smog chemistry as an early source of OH. Recent measurements of HNO_2 have employed conventional and annular denuders with a Na_2CO_3 coating, followed by aqueous extraction and either colorimetric or IC analysis for nitrite. Evidence for photolysis has also been presented, based on field measurements (11).

The recent development of a convenient method to generate HNO_2 has facilitated laboratory studies of HNO_2 (12). Laboratory tests at RTI have shown HNO_2 to respond as NO_2 on a CLM NO_x analyzer. Nitrous acid is not collected by Teflon filters; it appears to be quantitatively collected by both Na_2CO_3-coated filters and by triethanolamine (TEA)-coated filters; and it is collected up to a point by nylon filters (see Appendix A). Others have reported some retention of HNO_2 by nylon wool (13). Up to 12 μg of nitrite on nylon filters used for 4-hour sampling in the 1985 LA study and a diurnal cycle with high nitrite at night and low values during the day have been reported (8). This behavior coincides with the general trend for HNO_2 observed by others in that study, and provides supporting evidence that nylon collects HNO_2.

In a study conducted by RTI in the spring of 1986, annular denuders were used to sample for 24-hour and for 7-day periods. In most cases, the summed HNO_2 collected from seven 1-day samples exceeded that from the corresponding 7-day samples. In the same tests, the HNO_3 from the 7-day samples exceeded that from the summed 1-day samples. These results suggest collection of HNO_2 and conversion of NO_2^- to NO_3^- over time. In addition, it is not clear if HNO_2 can be produced by NO_2 in the sampler, particularly under high humidity conditions.

No method for the determination of HONO is sufficiently established to warrant recommendation at this time. Nevertheless, denuder and treated filter approaches both appear promising. The collected material, if nitrite, should be determined using IC or colorimetry.

NO_2--

Commercially available ambient air analyzers provide adequate sensitivity to measure NO_x in the relatively polluted atmospheres of urban and suburban areas, and in rural areas when the air quality is heavily influenced by plumes from vehicular traffic, power plants, or urban centers. Recently introduced high performance CLM NO_x analyzers have improved sensitivity and claim a detection limit of 0.5 $\mu g/m^3$ (14). In addition, the conventional CLM NO_x analyzer is not specific for NO_2: NO_2, HNO_3, HNO_2, and PAN all respond similarly, and as a result, cannot be distinguished by this method (15).

NO_2 is relatively difficult to collect efficiently using a chemically reactive surface (16). Coated filter samplers and denuders look promising but suffer from reduced collection efficiency under certain environmental conditions, or from a lack of specificity. Coatings of KI and $NaAsO_2$ can be used on denuders to collect NO_2 under humid conditions, but the collection efficiency is reduced under dry conditions, rendering this approach unsuitable for ambient sampling (see Appendix B). A TEA-based filter coating looks promising for collecting NO_2 (see Appendix A), but since both HNO_2 and PAN are interferents, it must be used to sample an air stream denuded of these compounds to provide specific information on the concentration of NO_2. In addition, this method has a flow rate limitation of 2 Lpm and must be used at temperatures above 5°C or collection of NO_2 will not be quantitative.

The most promising analytical techniques for use with chemically coated collection methods are spectrophotometric and ion chromatographic determination of nitrite. Both are well-established techniques.

The most promising currently available instrumental method for NO_2 is the LMA-3 Luminox NO_2 detector, produced by Scintrex of Ontario, Canada. A 0.01 $\mu g/m^3$ detection limit is claimed for this instrument (17). Tests in our laboratory have shown a nonquantitative interference by PAN (see Appendix D). Others have reported an extremely high temperature sensitivity (i.e., 4 percent/°C) and nonlinear response to NO_2 (18). At low NO_2 levels, ozone may also act as an interferent, and the instrument response is very sensitive to the "recipe" of the detection solution employed (19). Modifications have been reported by Scintrex which claim to resolve these problems. Nevertheless, in its current state, this method needs field validation and possibly additional development before it can be considered sufficiently reliable to be recommended for field deployment in rural environments.

SO_2--

Much like NO_2, commercially available ambient air analyzers provide adequate sensitivity to measure SO_2 only in the relatively polluted atmospheres of urban and suburban areas and in power plant plumes. Since the conventional instruments offer SO_2 detection limits of 10 $\mu g/m^3$, they are of little value in rural environments. A detection limit of 2.5 $\mu g/m^3$ is given for recently introduced high performance SO_2 analyzers, and developers claim that a new instrument with a lower detection limit can be produced (20).

Active samplers, such as coated denuders, filters, and sorbents, hold promise but also have disadvantages (16). Proper storage and handling are required to prevent contamination. Sorbents generally have sample flow limitations. Both coated filters and coated denuders offer good collection at relatively high flow rates, although coated filters can generally accomodate higher flow rates than even annular denuders. Sulfur dioxide is relatively easily collected, and the most promising types of collection media are carbonates and TEA coatings. While carbonate coatings have been tested and found satisfactory for most applications, they do suffer from reduced collection efficiency at humidities below 30 percent RH (21). In addition, Na_2CO_3 coatings are reported to require special care under high humidities to prevent dissolution of the carbonate (6). Humidity-related SO_2 recovery has also been noted with TEA-coated filters (see Appendix A).

Laboratory studies have shown SO_2 to be collected at least partially as SO_3^{2-} (see Appendix B). As a result, treatment of the extraction solution with H_2O_2 to oxidize the sulfite to the sulfate prior to analysis is recommended.

SO_2 detection methods are numerous, but many of them are costly and/or cumbersome to use. Two methods for detecting SO_2 as SO_4^{2-} that warrant further consideration are spectrophotometry and ion chromatography. Although IC is instrumentally fairly complex, it has adequate sensitivity and offers few interferences.

Carbonate-coated collection media should be considered for the collection of SO_2. At low (i.e., below 30 percent) relative humidities, a backup treated filter has been found effective for this application to insure quantitative collection. TEA should be considered as an alternate coating, although it displays a humidity influence and a flow rate limitation. It is recommended that IC be used as the analytical finish for determining collected SO_2 as SO_4^{2-}.

NH_3 and NH_4^+--

Since many analytical techniques do not differentiate between ammonia and ammonium ion, these two species must be separated during sampling, prior to analysis (22). A denuder tube for collection of ammonia gas, followed by a coated filter or sorbent for collection of particulate ammonium, appears to be the most promising method. Other ammonia collection methods must be preceded by a prefilter for collection of particulate ammonium ion. However, a significant amount of ammonia gas may be sorbed by the prefilter or acidic particles on the prefilter, and the particulate ammonium may undergo further reactions on the filter surface.

Several types of collection media have been studied. Nafion, a modifed Teflon film with sulfonic groups added through side chains for ion exchange, has been used as an ammonia-denuding surface (10). Coatings for denuder tubes and filters employing citric acid, oxalic acid, or phosphoric acid have also been used (23). They appear to be equally effective at collecting NH_3, although oxalic acid has an appreciable vapor pressure and may be partially lost from the coating substrate, due to volatilization.

The annular denuder, described previously (9) may be used to sample NH_3 and NH_4^+. For collecting ammonia, the coating used is citric acid. The denuder is followed by a Teflon filter to collect particles containing ammonium. Collected NH_4^+ may volatilize or remain on the Teflon filter, immobilized as a salt by collected acidic constituents.

A second recent innovation in the sampling of ammonia is the TFR (10). This device uses a Nafion strip as a partial denuder to remove a constant fraction of the gaseous NH_3 under transition flow conditions. The strip is followed by a Teflon filter, a nylon filter, and an oxalic acid-coated glass fiber filter. The total gaseous NH_3 is calculated from the analysis of the ammonium from the Nafion strip, and the particulate ammonium is then determined algebraically, using the ammonium found on the Teflon and oxalic acid-coated filters.

Many methods of ammonium analysis are available. Methods that warrant further investigation are colorimetry (24), ion selective electrode (ISE)(25), and IC (26). Colorimetric methods are sensitive but suffer from interferences, excessive reagent preparation, or reagent instability. Neither IC nor ISE are as sensitive as colorimetry (i.e., indophenol method), and ISE may suffer from interferences. IC requires fairly complex instrumentation but is selective and moderately sensitive.

The following approach is favored for the sampling and analysis of NH_3 and NH_4^+: use a denuder to collect gaseous NH_3, a filter downstream to collect NH_4^+-containing particles and a coated filter or denuder downstream to collect volatilized NH_4^+, and analyze the collected material using colorimetry or IC.

Particulate Nitrate (PN)--

The particle size distribution of PN is bimodal. PN is generally in the coarse size in marine environments, where ambient HNO_3 reacts with the coarse suspended sea salt (NaCl) to form $NaNO_3$ (27). Under other circumstances, the size distribution of PN will be determined by environmental conditions and the relative presence of precursors, including HNO_3, NH_3, and acidic aerosol, such as sulfates. For example, in the eastern U.S., during the summer, when the concentration of SO_4^{2-} is high, the temperature is high, and the NH_3 emissions are low, the $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$ equilibrium is shifted to the right.

This and metathetical reactions with acidic aerosols make gaseous HNO_3 available for reaction with and retention by coarse soil particles, giving rise to coarse PN. In contrast, some western urban areas (e.g., Los Angeles and Denver) have low SO_2 emissions, adequate NH_3 to neutralize acidic aerosol, and high concentrations of fine PN, presumably as NH_4NO_3.

The collection of particulate nitrates has been plagued by both positive and negative interferences (28). Many ambient sampling programs have used alkaline glass fiber filters for the collection of NO_3^-. This filter can sorb gaseous HNO_3 and promote the oxidation of gaseous NO_2 leading to the formation of artifact NO_3^- (a positive bias). Gaseous HNO_3 may be retained by reaction/sorption on particulate matter on the filter (a positive bias). Particulate nitrates may react with cocollected strong acids to release gaseous HNO_3 (a negative bias). Volatilization of collected NH_4NO_3 may occur from the filter (a negative bias). This is enhanced under unsealed and unrefrigerated storage conditions (29). High humidity conditions promote species interactions (bias, unknown direction).

The interaction of nitric acid with the filter or collected sample has been circumvented to some degree through the use of denuders. Gaseous nitric acid diffuses to the surface of the denuder and is collected by reaction with the collection media, while particulates pass through the device uncollected. An inert filter material is then used to collect the particulate matter. The three leading filter candidates are Teflon membranes, Teflon-coated glass fiber, and neutral or acid-treated quartz fiber filters. The latter is desirable since it permits higher flow rates; however, a precleaning procedure must be employed to remove the background NO_3^-. Since the inert particulate filter is still subject to the negative biases of liberated HNO_3 and volatilized NH_4NO_3, the resulting NO_3^- must be collected on a backup filter. Either nylon or NaCl-coated cellulose may be used as backup filters. Although pressure drop and capacity considerations favor the latter for high volume applications, due to the Cl^- peak, this collection method is incompatible with an IC finish.

It is recommended that the filters be extracted promptly after collection and the extract stored under sealed, refrigerated conditions prior to analysis. Aqueous solutions are used to extract NO_3^- species quantitatively in most of the analytical tecnhiques reviewed. The aqueous extract can be analyzed several ways. Most NO_3^- detectors demonstrate adequate sensitivity toward PN analysis due to the high sample loadings available. Although several techniques may be suitable, IC appears to be the technique of choice. It requires minimum sample extract manipulation; it is free of interferences; the sensitivity approaches that of colorimetric techniques; and it is amenable to measurement of nitrate loadings from both high and low volume samplers.

The following approach is recommended for sampling and analyzing fine PN in ambient air: use a cyclone or other suitable device to remove coarse particles that can act as potential sites for chemical interactions; use a denuder to remove HNO_3 prior to collection of fine PN; use a Teflon or other inert filter to collect fine PN; use a nylon or an alternate collection medium downstream of the Teflon filter to collect HNO_3 volatilized from the PN; extract filters promptly after sampling; store under refrigeration; and analyze the extract for NO_3^- by IC.

Particulate Sulfate (PS)--

Particulate sulfates usually occur in the fine size range and are on the order of 0.3 µm in diameter (28). Predominantly occurring sulfate species include H_2SO_4, NH_4HSO_4, and $(NH_4)_2\ SO_4$, with $CaSO_4$ and Na_2SO_4 to a lesser degree.

Speciation of sulfates is difficult. The filter alkalinity problems encountered in nitrate collection are also found in PS collection and lead to artifact SO_4^{2-} formation involving the conversion of SO_2 to SO_4^{2-} on alkaline glass fiber filters. Sulfuric acid aerosol neutralization is also likely to occur on such filters. In addition, the acid aerosol can be neutralized by cocollected particulate or gaseous material. For example, NH_3 can react with collected acidic aerosols, forming ammonium salts and altering the composition of the collected aerosol.

Problems attributable to filter alkalinity have generally been alleviated through the use of acid-treated or neutral quartz filters and Teflon filters. Sulfur dioxide interference appears to be minimal using either of these materials. Both Teflon and quartz show > 98 percent retention for SO_4^{2-} particles < 0.3 µm in diameter (30). Quartz filters may require cleaning before use. Their fragile nature presents a possible drawback for precleaning and normal handling associated with routine network operation.

High SO_4^{2-} loadings are normally available from high or low volume collection devices. Based on sensitivity considerations, several measurement techniques appear suitable, including IC, colorimetry, turbidimetry (and nephelometry), flame photometry, and X-ray fluorescence (28). The methyl thymol blue colorimetric technique appears to hold some promise. Sensitivity is adequate (especially for high volume sampling configurations), interferences are minimized, and automated methods are available. Ion chromatography has adequate sensitivity even for low volume samples, has good reproducibility, is free of interferences, requires little sample preparation, and is fairly rapid, while yielding information on other anions from the same chromatogram. As a result, IC is the method of choice for the determination of airborne sulfates.

The following approach is recommended for sampling and analyzing fine PS in ambient air: use a cyclone or other suitable device to remove coarse particles; use a denuder to remove NH_3 prior to the collection of fine PS; use a Teflon or other inert filter to collect fine PS; and extract the filters and analyze the extract for SO_4^{2-} by IC.

H^+ and Acidity--

Filtration of ambient aerosols appears to be the favored collection method for subsequent sample analysis for pH and acidity (31). The filter should be strong, inert, and efficient; it should be capable of high linear flow rates and should have low, consistent blank values. Teflon and pretreated quartz fiber filters appear to be satisfactory. The filter may be protected from gaseous NH_3, HNO_2, and HNO_3 by denuders. Removal of gaseous ammonia and nitric acid upstream of the filter, and reactions of the collected particulate with strong acids on the filter, can enhance volatilization and loss of collected NH_4NO_3 from the filter. Alteration of the particle catch by loss of NH_4NO_3 obscures the significance of the pH or acidity determination.

There are severe measurement problems for both pH and acidity, and there is a need for standardization of methods. The difficulty in accurately measuring the pH of a precipitation sample or a deposition solution arises from the low ionic strength of the sample and its effect upon the liquid junction potential of the reference electrode. The determination of total acidity is also subject to serious error in solutions of extremely low acidity.

One of the major problems in comparing deposition sample acidities determined by titration is that the titration procedures vary in detail. When a fixed pH endpoint technique is used, the amount of weak acid titrated will depend upon the endpoint chosen; thus, fixed pH endpoint titrations are not recommended for deposition analysis (32). Potentiometric titrations to an inflection point and Gran plots allow determination of both strong and weak acid components, respectively.

No method for the determination of pH and acidity of dry deposition is sufficiently established to warrant recommendation at this time. The major need in this area is a clear, objective statement that will define the rationale for pH and acidity determinations from dry deposition. This will permit definition of acceptability bounds for sampling and analysis methodologies, the approach to be employed in data interpretation, and the desired output(s).

O_3--

Many methods have been used for the determination of ozone, including colorimetry, fluorophotometry, chemiluminescence, IR or UV photometry, gas chromatography, and optical methods (33). Chemiluminescent and IR/UV spectrophotometric methods provide real-time, direct readout measurements, require no special collection procedures, are sensitive, specific and sufficiently rugged for field use. These instrumental methods are sufficiently developed and available commercially to meet the sampling and analysis needs of the acidic deposition research community.

A commercially available UV spectrophotometric continuous O_3 analyzer is recommended for sampling and analysis of O_3 in ambient air. The CLM continuous O_3 analyzer is less favored for field deployment than the above since an auxilliary compressed gas (ethene) is needed.

H_2O_2--

Of all oxidants considered important in atmospheric chemistry, H_2O_2 tends to concentrate most heavily in the liquid phase. In addition, the oxidation of S (IV) by H_2O_2 increases with decreasing pH. These considerations point toward H_2O_2 as a species of importance in the oxidation of atmospheric SO_2 (34).

Although collection methods such as scrubbers and bubblers have been used for trace gases, the most widely used method for collection of gaseous H_2O_2 from the atmosphere is purified, water-filled impingers (35). Among the interferents, NO_x, O_2, and O_3, ozone may be substantial because of its tendency to form H_2O_2 upon contact with water (36). Methods to minimize this problem through alterations in air-water contactor design (i.e., continuous, venturi, and diffusion scrubbers) and titration with NO are underway (37).

Although a research tool, a tunable diode laser absorption system (TDLAS) has been employed to determine H_2O_2 in the gas phase (38). Once in aqueous media, however, H_2O_2 can be determined in several ways by less elaborate means. One favored method is the horseradish peroxidase-catalyzed dimerization of p-hydroxyphenylacetic acid in the presence of H_2O_2 with fluorescent determination of the dimer (39).

The development of techniques for sampling and analyzing H_2O_2 in both gas and liquid phases from environmental samples is in the research mode. Although a commercial H_2O_2 monitor based on the horseradish peroxidase-mediated fluorescent (HPMF) approach is available, its specificity and reliability are unknown. Users suggest that it cannot be recommended at this time but may be in the future if operational difficulties are overcome and if field validation proves successful (40).

Three methods for determining ambient levels of H_2O_2 were involved in a field and an outdoor chamber intercomparison study in July of 1986 in Research Triangle Park, NC (41). Two of the methods used the HPMF approach but with different gas-liquid contactors, and the third involved the TDLAS. Results from this study should be available in early 1987 and should provide much useful information on the validity of the HPMF approach under realistic field conditions in the presence of a number of potential interferents. Nevertheless, no methods for H_2O_2 determination are sufficiently developed at this time beyond the research mode to warrant recommendation in an air monitoring network.

Organic Acids, RCOOH--

The gas and particulate phase distribution and approximate atmospheric concentrations define the parameters, such as sampling duration, sorbent capacities, and detection limits, required for collection and analysis of organic acids. Higher molecular weight carboxylic acids (i.e., C_{16} and greater) are primarily adsorbed on particles (42). Acids C_{13} and less are found primarily in the gas phase. Over 90 percent of particulate phase acids have been found on particles of less than 3 μm diameter, and individual species concentrations of up to 0.1 $\mu g/m^3$ have been reported (43). Organic acid concentrations are generally higher in the gas than in the particle phases. For example, formic plus acetic acid concentrations of 0.5 to 7 $\mu g/m^3$ have been reported in urban air (44). These acids may contribute significantly to free acidity of rainfall, but not to environmental acidification since they may be consumed quickly by microbes. The role of organic acids in the acidification of ecosystems is not well understood.

The collection strategy depends primarily on whether gas phase or particulate phase organic acids are targeted (45). No single sample collection scheme is available to cover the entire range of C_1 to C_{25} carboxylic acids in the atmosphere. High volume particle samples are usually collected on glass fiber filters. Air volumes of 600 to 10000 m^3 are required to provide sufficient material for extraction and analysis (42). One problem with high volume sampling is stripping of organic compounds from the collected particles, causing loss of lower molecular weight acids. Several schemes have been investigated for trapping low molecular weight organic acids, including solid sorbents, impingers with basic solutions, and condensate sampling. Liquid sampling solutions prevent loss of analytes, but can require large dilution volumes, present difficulties in handling and storage, and permit potential alteration of collected constituents.

Many techniques have been employed for separation and detection of organic acids: titration methods and gas, ion, and liquid chromatography. GC and IC are the most widely used approaches for separations. Particulate phase organic acids are usually solvent extracted and back-extracted to produce an "acid" fraction. The acids are then usually derivatized prior to capillary column GC analysis. This method is applicable to carboxylic acids from C_8 to C_{30}. Analysis of volatile C_1

to C_7 acids is more varied. Analysis by GC is the method of choice because it permits good separations with high sensitivity. To prevent problems associated with adsorption of acids, either the acid itself or the analytical system must be modified for successful analysis. The normal method is derivatization of the acid, usually esterification. Halogenated esters may be used to permit the increased sensitivity of electron capture detection. The GC columns may be modified by washing or conditioning procedures.

The development of techniques for sampling and analyzing organic acids in the particulate and gas phases from dry deposition samples is in the research mode. No methods for the determination of organic acids are sufficiently developed at this time to warrant recommendation for routine implementation in an air monitoring network.

Peroxyacetyl Nitrate, PAN--

PAN is a photochemical oxidant formed by the reaction of NO_2 with the peroxyacetyl radical, and may account for a significant portion of the tropospheric reservoir of nitrogen oxides. The peroxyacetyl radical can be formed by abstraction of a hydrogen from acetaldehyde followed by addition of oxygen. PAN acts as an organic sink for NO_2 much like HNO_3 acts as an inorganic sink for NO_x. Thus, measurement of PAN may provide insight into the photochemical history of an air parcel. PAN concentrations range from 0.05 to 1.0 $\mu g/m^3$ in unpolluted air, up to 50 $\mu g/m^3$ in urban air.

The currently favored method for PAN determination is gas chromatography with electron capture detection. Using cryogenic preconcentration, sensitivities as low as 0.05 $\mu g/m^3$ with ± 20 percent accuracy can be achieved (46). Since commercial PAN monitors are not available, elaborate equipment must be designed and built to permit continual monitoring. Species instability prevents integrated sampling. No methods for PAN determination are sufficiently developed at this time beyond the research mode to warrant recommendation for routine implementation in an air monitoring network.

Formaldehyde, HCHO--

Formaldehyde is the principal carbonyl compound in ambient air and a photolytically reactive intermediate in the tropospheric oxidation of methane and nonmethane organics to carbon monoxide. Thus, HCHO measurements may provide insight into the photochemical history of an air parcel. The distribution of HCHO between gas phase and liquid water is important since it may form an oxidation-resistant adduct with aqueous bisulfite, retarding the conversion of SO_2 to H_2SO_4 (47).

Integrated grab sampling, using a collection medium containing 2,4-dinitrophenylhydrazine and HPLC with UV detection as an analytical finish, appears to be a promising method (48). Two new continuous methods using fluorescent analytical finishes have recently been described (41). These two methods were compared with TDLAS in both field and outdoor chamber studies conducted in July of 1986 in Research Triangle Park, NC. Results from this study should be available in early 1987 and should provide useful information on the validity of these prototype methods for HCHO under realistic field conditions, in the presence of a number of potential interferents. Nevertheless, no methods for HCHO determination are sufficiently developed at this time beyond the research mode to warrant recommendation for routine implementation in an air monitoring network.

Multiple Constituent Systems

Currently, there are three multiple-constituent sampling systems that have been reported for collecting acidifying constituents from ambient air. They are the filter pack (FP), the transition flow reactor (TFR), and the annular denuder system (ADS). For each system, the species sampled for subsequent analysis are given in Table 4.

FP--

The filter pack approach is employed in networks operated by Environment Canada and the Ontario Ministry of the Environment (7,8, 49). The system consists of a three-stage filter pack sampling at approximately 20 Lpm. An open-face 2 μm pore size Teflon filter is the first element, followed by a 1 μm pore size nylon filter, followed by

TABLE 4. SUMMARY OF MULTIPLE CONSTITUENT SAMPLING SYSTEMS AND SPECIES SAMPLED

Species	System		
	FP	TFR	ADS
HNO_3		X	X
HNO_2			X
NO_2		X	
SO_2	X	X	X
NH_3		X	X
NH_4^+	X	X	X
NO_3^-		X	X
$HNO_3 + NO_3^-$	X	(X)	(X)
SO_4^{2-}	X	X	X
H^+/Acidity	X	X	X

an impregnated (K_2CO_3 and glycerin) Whatman-41 filter. The filter size is approximately 47 mm in diameter. Since open-face filters are used, sampling is not size selective. The extract from the Teflon filter is analyzed by IC for SO_4^{2-} and NO_3^-, by IC in one network and by colorimetry in the other for for NH_4^+, and by colorimetric titration for acidity. The nylon filter is extracted in 0.003 N NaOH and analyzed by IC for NO_3^- and SO_4^{2-}. The impregnated Whatman-41 filters are analyzed for SO_4^{2-} by IC which is added to that recovered from the nylon filter and reported as SO_2.

The FP has a number of limitations:

a. As a result of potential positive and negative biases in HNO_3 and particulate NO_3^- sampling, the sampler does not provide HNO_3 concentration data. The sum of the NO_3^- from the Teflon and nylon filters represents Total Inorganic Nitrate (TIN).

b. The presence of acidic particles on the Teflon filter offers the potential for neutralization and change in speciation of acidic sulfates when NH_3 is present in sampled air.

c. The system does not permit the determination of gaseous NH_3. As a result, it also offers the potential for high bias of particulate NH_4^+ estimates derived from Teflon filter extracts.

d. The potential biases in nitrate sampling, coupled with the potential neutralization of acidity by gaseous NH_3, make interpretation of H^+/acidity data from the Teflon filter extract difficult.

e. The system does not permit the determination of HNO_2. However, if HNO_2 is transmitted by the Teflon filter, then it should be retained on the nylon and K_2CO_3-coated filters.

f. Sulfate collected on the nylon and impregnated Whatman-41 filters must be summed to infer SO_2 concentration, since nylon can collect SO_2 as SO_4^{2-}.

g. Since the approach does not employ size selective sampling, distinction of the distribution of chemical constituents between coarse and fine particles is not possible.

The FP has advantages which include simplicity, low cost of deployment, and high sensitivity. The FP approach has been used in different configurations for network sampling in Canada since the late 1970's. Thus, of the systems considered, the FP has the largest historical data base.

TFR--

A multiple constituent system incorporating transition flow reactors and filter collection media has been designed (10). As shown in Figure 1, the TFR system is comprised of modules arranged in series to collect various constituents of interest. The first module is a Teflon cyclone having a D_{50} (ρ = 1.0) of 1.8 µm at 33.2 SLPM and of 2.5 µm at 17.3 SLPM. The second and third modules are two TFR for determination of HNO_3 and NH_3, followed by a filter pack containing a 2 µm pore size Teflon filter, a 1 µm pore size nylon filter, and an oxalic acid impregnated glass fiber filter. The first TFR uses a nylon strip as a partial denuder to remove a constant fraction (i.e., 8.5%) of gaseous HNO_3 under transition flow conditions. The second TFR uses a Nafion strip as a partial denuder to remove a constant fraction (i.e., 17%) of gaseous NH_3. The subsequent Teflon and nylon filters collect PS, PN, and HNO_3 vapor. PS is determined from the analysis of sulfate from the

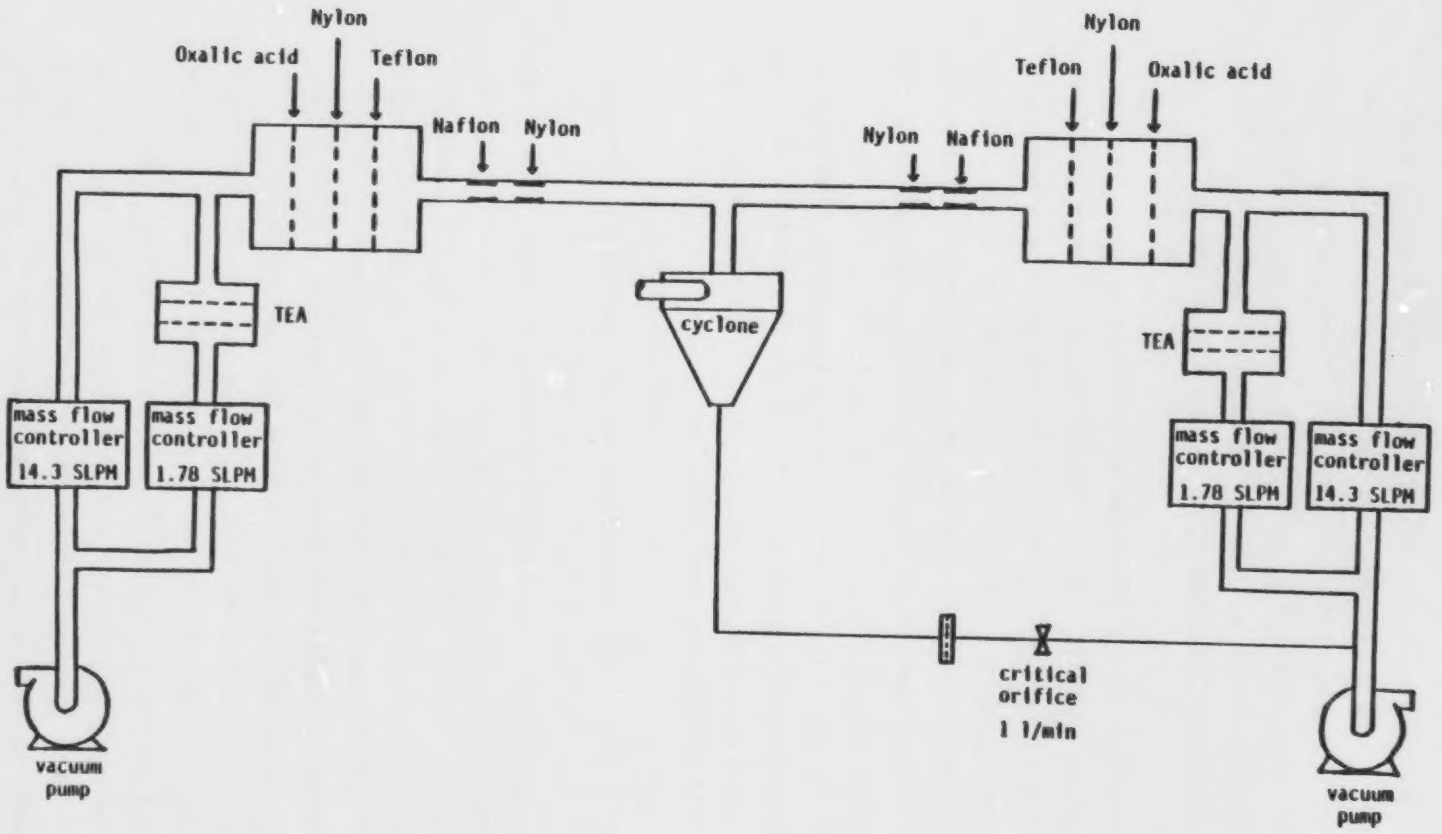

Nylon
Oxalic acid
Teflon
Naflon
Nylon
Nylon
Naflon
Nylon
Teflon
Oxalic acid
TEA
cyclone
TEA
mass flow controller 14.3 SLPM
mass flow controller 1.78 SLPM
mass flow controller 1.78 SLPM
mass flow controller 14.3 SLPM
critical orifice
1 l/min
vacuum pump
vacuum pump

Figure 1. Transition flow reactor sampling system.

Teflon filter. The total gaseous HNO_3 is determined from the analysis of nitrate from the nylon strip, and the PN is then determined algebraically, using the nitrate found on the Teflon and nylon filters. The total gaseous NH_3 is determined similarly, using the analysis of ammonium from the Nafion strip, and the particulate ammonium is found algebraically, using the ammonium found on the Teflon and oxalic acid coated filters.

Downstream of the filter pack, the flow splits with 14.3 Lpm to a mass flow controller and pump, while 1.8 Lpm passes through two TEA-coated glass fiber filters for collection of SO_2 and NO_2. This low volume stream then passes to a mass flow controller and pump. A third flow stream at a nominal rate of 1.0 Lpm is drawn from the base of the stagnation zone of the cyclone to prevent particle accumulation in the event of heavy particle loading.

The concept of operating a sampler in the transition flow regime from a fluid dynamics perspective seems tenuous. The transition regime is an unstable condition where the fluid can be laminar flow or turbulent, or oscillate between the two (50). In addition, operation in such a regime may make the type of flow conditions that exist during sampling susceptible to hardware differences and operational perturbations.

The TFR has been under development for several years. The first reported test results were obtained in 1983. Published results show good reproducibility for the TFR which appear to allay the concerns expressed above (10). Recent results from a network, however, suggest that over 30 percent of the time, the HNO_3 found on the nylon strip exceeded the theoretical physical bound of 8.5 percent and 20 percent of the time this bound was exceeded by more than 100 percent (51). Examination of replicate samples from this data set showed that the bound was exceeded for one of the replicate samples 25 percent of the time and for both of the replicates 25 percent of the time. As with any developing method, operational and procedural difficulties may be responsible for these findings, since similar problems were not noted by the developers but have arisen upon implementation by less skilled personnel (52). Nevertheless, these findings point toward the need for more extensive field testing to validate the method.

The TFR has a number of limitations:

a. The system does not permit the determination of HNO_2.

b. Nitrates collected in the cyclone and not removed during sampling may volatilize to give artificially high values of gaseous nitric acid.

c. HNO_2 may be collected to some extent on the nylon filter, while the remainder is likely to be collected on the TEA-coated filters, acting as a positive bias.

d. The collection of PAN on TEA may provide a positive bias for NO_2 determinations.

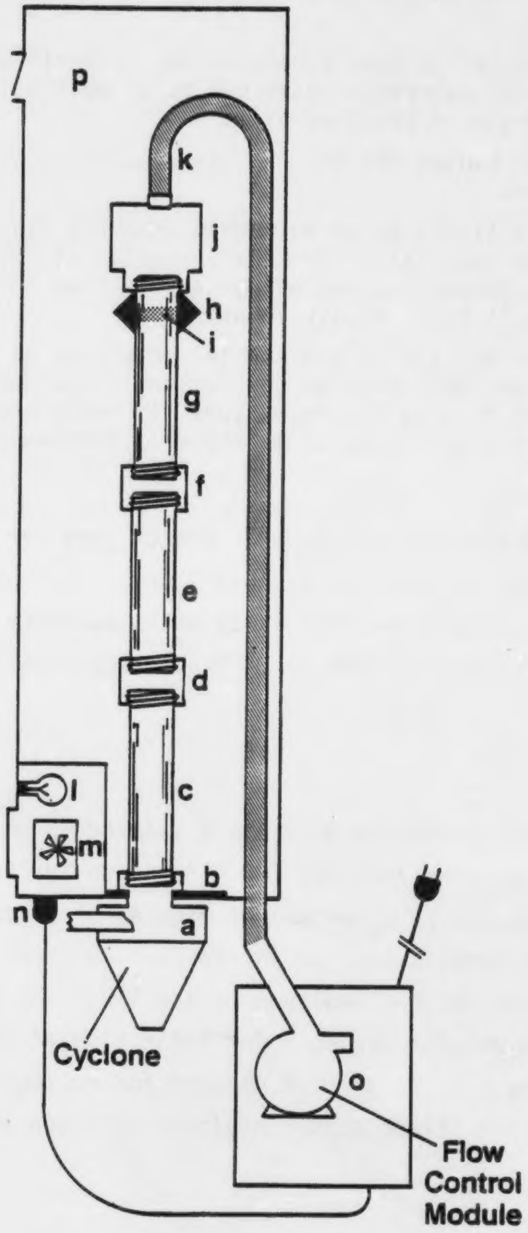
e. Sulfur dioxide is likely to be collected on currently available nylon filter materials. If this retention of SO_2 is significant, SO_2 determinations using results from the TEA-coated filters will require adjustment.

f. The potential for deposition and partial retention of acidic and basic gases and particles on the Teflon filter makes interpretation of acidity determinations difficult and may prevent unambiguous inference of atmospheric particulate constituents.

The TFR has advantages which include: it can be used for sampling dry deposition constituents for periods of 1 to 7 days; it is modular, easy to install and ship; sample analysis is by existing, accepted methods (i.e., IC and colorimetry); and it is reasonably simple to operate.

ADS--

A multiple constituent system incorporating annular denuders and filter collection media has been designed (9). As shown in Figure 2 (also see Appendix C), the ADS is comprised of modules arranged in series to collect various constituents of interest. The first module is a Teflon cyclone similar to that employed by the TFR. The second and third modules are two annular denuders for collection of HNO_3, HNO_2, and SO_2, followed by a third annular denuder for collection of NH_3. The fifth element is a filter pack containing a Teflon and a nylon filter.


p
k
j
h
i
g
f
e
d
l
c
m
b
n
a
Cyclone
o
Flow
Control
Module

a. TFE Teflon cyclone
b. Aluminum shield
c. Na_2CO_3-coated denuder
d. Teflon coupling
e. Na_2CO_3-coated denuder
f. Teflon coupling
g. Citric acid-coated denuder
h. Support bracket
i. Velcro fastener
j. Filter pack
k. Flow line
l. Light bulb
m. Fan
n. Electrical connection
o. Flow control module
p. Sampler box

Figure 2. Annular denuder sampling system.

The nominal sampling rate is 15 Lpm. Ambient air is passed under laminar flow conditions through the annular space of two concentric tubes. The outside of the inner tube and the inside of the outer tube are coated with a specific gas-absorbing solution. For the first two denuders, this coating contains Na_2CO_3; for the third denuder, the NH_3-absorbing coating contains citric acid. The annular design permits a reduction in denuder tube length and an increase in flow rates over the conventional open-tube denuder design. The third denuder is followed by a Teflon filter to collect PS, nonvolatilized nitrates, and particulate ammonium, while the nylon filter collects HNO_3 that is passed due to volatilization from the Teflon filter. A third filter may be added downstream of the nylon filter to collect any volatilized ammonium.

HNO_3 and SO_2 are determined from the differences between IC analyses of NO_3^- and SO_4^{2-} in the aqueous extracts of the first and second denuders. Analysis of the second denuder extract confirms the near quantitative collection of these species and permits a quality control check.

HNO_2 is deposited nearly quantitatively on the first denuder. Deposition of PAN and NO_2 have been found to range from 1 to 3 percent (see Appendix B). Since deposition of these two species is very small on the first denuder, the deposition should be approximately the same on the second denuder. The recovery of HNO_2, PAN, and NO_2 as NO_2^- on the first two denuders, and the low deposition of the latter two species, permits the determination of HNO_2 by using the difference in NO_2^- between the first two denuders. Extract analysis can be performed by either IC or colorimetry.

NH_3 and NH_4^+ are determined from colorimetric NH_4^+ analysis of the aqueous extract of the citric acid-coated third denuder and Teflon filter, respectively. PS and nonvolatilized nitrates are determined by IC analysis of SO_4^{2-} and NO_3^- in the aqueous extract of the Teflon filter. Nitrate analysis of the 0.003 N NaOH extract of the nylon filter permits determination of volatilized nitrates. Fine PN is determined by summing the nonvolatilized and volatilized nitrates.

The concept of an open channel laminar flow denuder is well-accepted, and the deployment of such devices has been used widely for selective gas sampling for many years (1,5). The adaptation of the open cylindrical channel approach to that of an annular space, with its inherent increase in permissible sampling rate, was initially reported in 1983 (9). This approach was first used in the U.S. in the spring of 1985 (23). Since that time, several prototype versions of the ADS have been developed and tested. Consideration of the ADS for determining various atmospheric constituents is based on promising results of recent tests (23,53) and the acceptance of traditional open channel denuders in related applications.

The ADS has several limitations:

a. The system does not permit the determination of NO_2.

b. Care must be taken at high humidities to prevent dissolution and loss of capacity of Na_2CO_3 denuder coatings, and data must be inspected at low humidities to insure good collection efficiencies.

c. The collected HNO_2 may undergo *in situ* oxidation to nitrate on the first denuder, giving rise to artificially high values for HNO_3 and low values for HNO_2.

d. Nitrates collected in the cyclone and not removed during sampling may volatilize to give artificially high values of gaseous nitric acid.

e. The loss of HNO_3 by volatilization from the Teflon filter makes interpretation of the acidity determinations difficult.

f. In the absence of an NH_3 collection medium such as a coated filter downstream of the nylon filter, a portion of the volatilized particulate NH_4^+ may be lost.

The ADS has advantages: it can be used for sampling dry deposition constituents for periods of hours to 7 days; it is modular, easy to install and ship; sample analysis is by existing, accepted methods (i.e., IC and colorimetry); and it is reasonably simple to operate.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The chemical-specific sampling and analysis methodologies for many chemical constituents of importance in ecosystem acidification have been reviewed and evaluated. Their status is summarized in Table 5. The "recommended" designation means that, in the author's opinion, the method is sufficiently developed to warrant routine implementation in an air monitoring network. The "favored" designation means that the method, at its current state of development, holds promise for providing unambiguous concentration data for the species of interest and for achieving routine implementation in an air monitoring network. Where no designation was given, insufficient information is available to permit a status assessment.

Recommended methods are given for four species: HNO_3, NO_3^-, SO_4^{2-}, and O_3. The bulk of the methods are designated as "favored," while two (i.e., RCOOH and HCHO) are in the research mode, and no assessment can be made at this time. For some species, well-established methodologies may exist (e.g., FTIR and TDLAS), but their resource and/or manpower requirements prevent them from consideration in network application. In these cases, such devices are not listed in Table 5.

The selection of a multiple constituent sampling system is not clear. The FP can provide estimates of concentrations of total inorganic nitrate, total particulate sulfate, and SO_2 and biased estimates of particulate NH_4^+ and acidity at a relatively low potential cost. The TFR and ADS offer estimates of a larger number of constituents but at a larger potential cost. The ADS can provide concentration estimates of HNO_2, but not NO_2; whereas the TFR can provide NO_2, but not HNO_2. Although successful field trials have been reported for the TFR, successful deployment for measuring HNO_3 and fine particulate NO_3 was not realized by RTI in the field study described in the main body of this report. As a result, the TFR can

TABLE 5. Status of Chemical-Specific Sampling and Analysis Methods for Dry Deposition

	Sampling Technique			Analysis Technique			
Species	Type	Method	Status	Species	Method	Status	Comments
HNO_3	I	Denuder (Annular or open channel)	R	NO_3^-	IC	R	Collection media of carbonates, MgO, or nylon appear suitable; this sampling method can be a denuder difference (which is not recommended due to flow limitations) or an annular denuder (ADS).
	I	Nylon strip denuder (TFR) + nylon filter	F	NO_3^-	IC	R	
HNO_2	I	Denuder	F	NO_2^-	IC or Col	R	Carbonate collection media appears suitable; both methods need additional testing; oxidation of collected nitrite to nitrate may present artifact problems.
	I	Coated filter	F	NO_2^-	IC or Col	R	
NO_2	C	Instrumental (LMA-3)	F	—	CLM	F	No sampling methods for NO_2 can be recommended without additional development, since none appear specific for NO_2; LMA-3 is very sensitive; conventional CLM instruments display inadequate sensitivity and are not favored; high performance CLM instruments are favored in spite of marginal sensitivity; all three methods are subject to NO_x interferences.
	C	Instrumental (high performance)	F	—	CLM	F	
	I	TEA-coated filter	F	NO_2^-	IC or Col	R	
SO_2	I	$CO_3^=$ coated filter or denuder	F	SO_4^{2-}	IC	R	High or low humidities may adversely affect collection efficiency of carbonate; TEA-coated filter is restricted to low flow rates and may require humidity correction; conventional instruments may be favored if their marginal sensitivity can be improved.
	I	TEA-coated filter	F	SO_4^{2-}	IC	R	
	C	Instrumental	—	—	Pulsed fluorescence	—	
NH_3	I	Citric acid coated denuder (ADS)	F	NH_4^+	Col	R	Collection media of citric acid, oxalic acid, phosphoric acid or naphion appear suitable.
	I	Naphion strip denuder (TFR) + coated filter	F	NH_4^+	Col	R	
NH_4^+	I	Denuder + Teflon filter + coated filter	F	NH_4^+	Col	R	Denuder needed to remove NH_3; NH_4^+ collected on Teflon filter; coated filter needed to collect NH_4^+ volatilized as NH_3.
NO_3^-	I	Denuder(s) + Teflon filter + nylon filter	R	NO_3^-	IC	R	Denuders needed to remove HNO_3 and NH_3; NO_3^- collected on Teflon filter; a nylon filter is needed to collect NO_3^- volatilized as HNO_3.
SO_4^{2-}	I	Denuder + Teflon filter	R	SO_4^{2-}	IC	R	A denuder is needed to remove NH_3.
	I	Teflon (or quartz) filter	F	SO_4^{2-}	IC	R	Method may be subject to bias from SO_2 oxidation on collection medium.
H^+/Acidity	I	Denuders + Teflon filter	F	H^+	pH meter; titration	F F	Titration is needed to distinguish strong and weak acids; volatilization losses from Teflon filter make data interpretation difficult.
O_3	C	Instrumental	R	O_3	UV photometry	R	Instrument commercially available.
H_2O_2	C	Instrumental	F	—	Fluorescence	F	Continual horseradish peroxidase mediated fluorescent method is favored but needs development and testing.
PAN	C	Instrumental	F	PAN	GC-EC	F	Instrument must be fabricated on a custom basis by user.
RCOOH	I	Denuder + high volume filter	—	—	GC, LC, IC	—	A successful approach may involve separate collection of vapor and particulate phases followed by extraction, derivatization, and analysis.
HCHO	I	Coated collection surface	—	—	HPLC-UV	—	Collection medium of 2,4-dinitrophenylhydrazine followed by detection of the HCHO-hydrazone.
	C	Instrumental	—	—	Fluorescence	—	

Abbreviations:	I	Integrated sample
	C	Continuous or continual sample
	R	Recommended
	F	Favored
	IC	Ion chromatography
	Col	Colorimetric
	CLM	Chemiluminescence

not be endorsed for HNO_3 or fine particulate NO_3^- measurements at this time. From an operational perspective the ADS is marginally preferable to the TFR. Thus, while the available evidence does not provide overwhelming support for the selection of either the TFR or the ADS for deployment in an air monitoring network, on balance the ADS does appear to have a slight advantage over the TFR. Additional development and field tests are recommended to provide the comparisons necessary to assess the merits of two sampling systems more clearly. It is also recommended that data quality objectives (DQO's) be clearly established for the species of interest. This will permit selection of a sampling system that is optimized to meet user needs.

The main body of this report as well as Appendix G have focused on the analysis and discussion of results of a methods comparison study conducted in the fall of 1986 by RTI and others at the EPA dry deposition site at RTP, NC. This study consisted of 13 daily samples; weekly data were also collected with the ADS. The term TFR normally refers to the TFR system operated daily by RTI throughout the study; TFR(EPA) refers to the TFR operated by EPA/ASRL on 5 of the 13 study days. The study plan relied on TFR results from the EMSL-operated EPA network station. These data are not available for inclusion in this report. Conclusions and findings drawn from this study are given below.

- Based on replicate analyses of quality control solutions and authentic field samples and on interlaboratory comparisons across four laboratories, analytical precision for the determination of NO_2^-, NO_3^-, and SO_4^{2-} were good (i.e., 5 percent or better). Ammonium determinations were more variable (i.e., 15 percent). No analytical bias was apparent for any of the above species.

- Detection limits for the ADS and TFR are generally less than 0.15 ppb, except for NH_3 with the ADS at 0.4 ppb and for SO_2, NO_2, and NH_3 with the TFR at 0.4, 0.5, and 1.6 ppb.

- Both ADS and TFR show good precision for all measured species concentrations except fine particle NO_3^-. In all cases the median difference between paired daily ADS samples is less than 0.2 $\mu g/m^3$, and median CV's are less than 16 percent. In all cases the median CV's for paired weekly ADS samples are less than 18 percent. Except for NO_2 and SO_2, the median difference between paired daily TFR samples is less than 0.5 $\mu g/m^3$. Except for HNO_3 and H^+, the median CV's for daily TFR samples are less than 14 percent.

- Nitric acid spiking experiments showed good recovery of nitrate by extracting and analyzing all parts of ADS and TFR samplers. The nitric acid spiking rate was accurately estimated by the ADS but was overestimated by the TFR. Substantially more variability is apparent in the TFR estimates of ambient HNO_3 than in the ADS results (i.e., CV's of 21 versus 8 percent). Quality control checks indicate ambient TFR HNO_3 and fine particulate NO_3^- results to be suspect. In 24 of 26 cases TFR Fine NO_3^- results were negative. This invalidated TFR Fine NO_3^- results and prevented their use in subsequent analyses. Thus, results of the current study do not permit the endorsement of the TFR for the determination of HNO_3 or Fine NO_3^-.

- Quality control checks do not indicate TFR(EPA) results for HNO_3 and Fine NO_3^- (NH_3 was not measured) to be suspect for the five daily tests. Quality control checks do indicate TFR(EPA) results for HNO_3 and Fine NO_3^- to be suspect for one of the two weekly samples.

- For the two stable species, total particulate sulfate (Total SO_4^{2-}) and total gaseous and particulate nitrate (Total NO_3^-), the results from the ADS and TFR are highly correlated, have average ratios near unity, and are not significantly different. These findings indicate that both samplers were operating under known flow conditions.

- Total NO_3^- as measured by the ADS, TFR, and FP are in good agreement. Total SO_4^{2-} as measured by the ADS, TFR, and FP are also in good agreement. This means that for these two parameters, the differences between the results of the FP and either the ADS or TFR are not significant at the 95 percent confidence level.

- Statistical comparisons of ADS and TFR results show no difference for Total NO_3^-, particulate NO_3^- on Teflon filters, Total SO_4^{2-}, and NH_3; the ADS estimate to exceed that of the TFR for Fine SO_4^{2-}, SO_2, and H^+; and the TFR estimate to exceed that of the ADS for HNO_3, Total $NH_3+NH_4^+$, and Fine NH_4^+.

- Nitric acid spiking experiments indicate that appreciable amounts of HNO_3 may be retained by Teflon cyclones, and that HNO_3 transmission approaches 100 percent for some types of Teflon after a brief conditioning period.

- A substantial difference in particle collection efficiency by the ADS and TFR cyclones resulted from sampling at different flow rates. This is most apparent for particulate nitrates where the cyclone catch accounted for 59 percent of the total in the ADS and 85 percent in the TFR. It is also apparent for fine particulate SO_4^{2-} where the results from the ADS exceed those from the TFR by approximately 5 percent. It is recommended that identical inlet particle conditioning be employed in any future sampler comparisons and that the conditioning device be extracted and analyzed for the species of interest.

- A cyclone bleed stream was not needed on daily TFR samples.

- Denuding the sampled atmosphere of all the gaseous HNO_3 and NH_3 in the ADS caused substantial volatilization of collected fine particulate nitrates: 52 percent for daily samples and 93 percent for weekly samples. This and the difference in cyclone efficiencies prevent meaningful direct comparison of nitrates on the Teflon filter for the ADS and TFR.

- Partial denuding of gaseous HNO_3 and NH_3 resulted in small volatilization of collected fine particulate nitrates in the TFR. This permits the use of the sum of the nitrate on the nylon strip and filter to estimate an upper limit on the HNO_3 concentration assuming that the TFR functions similarly to an FP. Nitric acid estimates using this approach and designated TFR (FP) show better agreement with ADS measures of HNO_3 than do estimates based on TFR theory.

- Nitric acid, as measured by the ADS, FP, and TFR(FP), a nonstandard interpretation of TFR data, are in good agreement with those of the TDLAS (i.e., the differences between the TDLAS results and those of each of the three listed measures are not significant at the 95 percent confidence level). Two sets of TFR results were collected by independent operators (RTI and EPA). Differences between TDLAS results and one of the TFR results are significant. The daily TFR results are consistently much higher than those of the TDLAS. The five daily TFR(EPA) measures of HNO_3 are also consistently higher but are in better agreement with TDLAS results.

- Nitrogen dioxide as measured by the TFR and TDLAS are highly correlated although differences between the two sets of results are statistically significant.

- Weekly average concentrations computed from measured daily samples were ratioed to measured weekly results to assess ADS sample stability. The ratio was near unity for most species. High ratios for NO_3^- on Teflon filters and for HONO reflect enhanced volatilization of NO_3^- from Teflon filters and enhanced NO_2^- oxidation on the denuders over 1-week versus 1-day sampling periods. The conversion of nitrites to nitrates over extended sampling periods (i.e., weekly periods) may result in an overestimate of ambient HNO_3 concentrations and an underestimate of ambient HONO concentrations with the ADS.

- Both nitrate and ammonium are volatilized from the ADS Teflon filter. A nylon filter is employed downstream to collect volatilized nitrate. The ADS, as operated with no provision to collect volatilized NH_4^+, undersamples particulate NH_4^+. It is recommended that a citric acid-coated filter be incorporated in the ADS to collect volatilized ammonium.

- The sum of gaseous NH_3 plus particulate NH_4^+ concentrations as measured with the TFR exceed those with the ADS.

- Total particulate NH_4^+ as measured by the TFR and FP are in good agreement and exceed measurements with the ADS.

- H^+ concentrations measured with the ADS exceed those with the TFR because undenuded NH_3 in the air sample reaching the TFR Teflon filter neutralizes a portion of the H^+ collected on the Teflon filter with that sampler.

- The ratios of measured cations to anions on the Teflon filters approach unity in the daily ADS and TFR samples. This ratio is less than unity for weekly ADS samples and substantially less than unity in cyclone extracts from daily and weekly samples. This suggests the presence of unmeasured ions. Crustal salts in the large particle size range may account for the findings in the cyclone extracts.

- Nylon filters in the TFR were found to retain a relatively constant amount of SO_2 (i.e., 0.47 µg SO_4^{2-}/m^3 or 10 µg/filter). This should be considered when determining SO_2 from daily samples using the TFR.

- SO_2 concentrations measured with the ADS exceed those measured with the TFR by approximately 30 percent. Laboratory tests suggest that the TFR results require a correction for reduced SO_4^{2-} recovery efficiency (i.e., 80 percent) under humid conditions.

- Nitrite was not recovered from TFR nylon filters. This suggests that sampled HONO is removed upstream of the nylon filter in the TFR, is not collected by the nylon filter, or is not recoverable from the nylon filter.

- Comparison of the fine particulate NH_4^+ and SO_4^{2-} data collected with the ADS in Los Angeles and in RTP, NC shows excess fine particulate NH_4^+ present in LA and excess fine particulate sulfate in NC. The extent of excess sulfate in NC appears to be strongly dependent on season.

- Field studies have demonstrated that the ADS can be successfully deployed for sampling periods of 4, 6, 10, 12, and 22 hours, and up to 7 days. The results are subject to a potential high bias for HNO_3 (from HONO oxidation) and a low bias from inlet losses and to low biases for HONO and NH_4^+ (if a citric acid-coated filter is not added). Field studies have demonstrated that the TFR can be successfully deployed for sampling periods of 22 hours and 7 days. The results are subject to a low bias for SO_2 (if SO_2 collected on the nylon filter and a recovery efficiency correction are ignored). TFR results may be unreliable for HNO_3 and Fine NO_3^-. These findings, although favoring the ADS, do not permit the complete endorsement of either the ADS or the TFR for field deployment without further development and field testing.

SECTION 3

EXPERIMENTAL

Two field evaluations of dry deposition methodologies were conducted between August and December 1986. The Research Triangle Institute (RTI) participated in both studies. The first study involved weekly collocated sampling where two ADS samplers were operated simultaneously for 7-day periods over approximately 3 months from 8/26/86 to 12/02/86. Sampling was conducted at the dry deposition monitoring station at a site adjacent to an EPA research facility in the Research Triangle Park (RTP), NC. The main objective was to collect data that would permit evaluation of the feasibility of sustained field operation of the ADS.

A second, more intensive, field evaluation study was planned and organized by the Monitoring Methods Section (MMS) of the Environmental Monitoring Systems Laboratory (EMSL) of EPA. This study involved RTI and several other participants. Measurements using a number of methods were made at the RTP site for comparison. Daily sampling was performed over 13 consecutive days beginning on 09/29/86 and ending 10/12/86. During the study, RTI operated two ADSs and two TFRs; analyzed samples from the ADSs, TFRs, and two FPs; and conducted special studies.

The bulk of the data collected by RTI in these studies is listed in Appendix F. Results of RTI's participation in these studies are described and discussed in the main body of this report. A preliminary assessment of the results of the second study including across-methods comparisons is given in Appendix G.

The ADS is described in Section 1.0, Reference 9, and Appendix C. In this device, sampled air passes in series at 14 SLPM through: a cyclone to remove large particles; two Na_2CO_3 coated annular denuders to collect HNO_3, HONO, and SO_2; one citric acid coated annular denuder to collect gaseous NH_3; one Teflon filter to collect

Preceding page blank

fine particles; and one nylon filter to collect volatilized nitrate. In four of the 1-week tests a citric acid coated filter was added downstream of the nylon filter to collect volatilized ammonium.

The TFR is described in Section 1.0 and Reference 10. Air is sampled at 33 SLPM through a cyclone of the same design employed in the ADS; the sample is then split into two identical trains. A 1 SLPM bleedstream is drawn from the cyclone base to prevent particle accumulation. This stream passes through a Na_2CO_3 coated filter to permit resolution of nitrates and sulfates. Each 16 SLPM stream passes through a tube lined with a 3.2 cm long strip of nylon and similar strip of Nafion to collect 8.5 and 17 percent of the respective gaseous HNO_3 and NH_3. The sample then passes through a Teflon filter to collect fine particles, a nylon filter to collect the remaining HNO_3 and volatile nitrate, and an oxalic acid coated filter to collect the remaining NH_3 and volatile ammonium. At this point a 1.6 SLPM stream is drawn through two triethanolaminine (TEA) coated filters to collect SO_2 and NO_2. This 1.6 SLPM stream and the remaining 14.4 SLPM stream then pass through mass flow controllers (MFCs) and are exhausted through a pump.

The samples collected in the ADS, TFR, and FP are extracted into solution where the recovered ions are analyzed. Nitrate, nitrite, and sulfate are determined by ion chromatography (IC). Ammonium is determined by a colorimetric method, indophenol blue. Hydrogen ion concentration is determined as pH. The measured mass of each species is used along with the sampled volume of air to infer the airborne concentration.

SECTION 4

RESULTS AND DISCUSSION

This section is comprised of two subsections. The first describes the results of quality control and quality assurance activities performed during the study. The second focuses on the results of special studies, ranging from individual topics associated with the operation and performance of the ADS and/or the TFR to comprehensive comparisons of the results of the ADS and TFR. Across-methods comparisons of all methods used in the Fall 1986 intensive field study are discussed in Appendix G.

QUALITY ASSURANCE AND QUALITY CONTROL ACTIVITIES

Analysis of Quality Control Solutions

Quality control (QC) solutions for NH_4^+, NO_2^-, NO_3^-, and SO_4^{2-} were prepared independently of the routine calibration standards. The concentrations of these QC samples were chosen to be representative of those found in authentic environmental samples. Aliquots of these QC solutions were analyzed daily by IC, while the NH_4^+ colorimetric analyses were performed randomly. Based on these analyses, the concentration of each species found was compared with the amount expected, and a percent recovery and standard deviation were calculated for each species. The results summarized in Table 6 show quantitative recovery with good precision and suggest that there was no bias in the analytical results.

Replicate Analyses

Eight sets of random samples were selected for replicate analyses. Each replicate analysis for NO_2^-, NO_3^-, and SO_4^{2-} was performed on the same day as the initial analysis, while each replicate NH_4^+ determination was performed approximately two weeks later.

TABLE 6. RESULTS OF ANALYSIS OF QC SOLUTIONS

Species	Analytical Method	Number of Analysis	Recovery Percent[a]	
			$\bar{x}$	s
NO_2^-	IC[b]	64	99.54	4.54
NO_3^-	IC	64	98.98	4.42
SO_4^{2-}	IC	65	99.53	4.05
NH_4^+	Colorimetry[c]	8	98.68	14.51

[a] $\text{Recovery} = \frac{\text{(Species Concentration Found)}}{\text{(Species Concentration Expected)}}$

[b] IC = ion chromatography

[c] Colorimetry = indophenol blue method

TABLE 7. SUMMARY OF REPLICATE ANALYSES

Species	NO_2^-	NO_3^-	SO_4^{2-}	NH_4^+
Overall				
n	30	34	28	20
$\overline{CV}$[a]	5.14	4.84	3.60	17.04
Upper Quartile				
$\overline{CV}$	1.92	1.39	1.56	3.48
Lower Quartile				
$\overline{CV}$	4.98	8.64	6.94	18.33
Concentration[b]	0.10	0.13	0.46	0.79

[a] Percent.

[b] Concentration at beginning of lower quartile, expressed in μg/ml.

For each pair of data, a mean and a coefficient of variation (CV = 100 x standard deviation/mean) were computed. The averages of the individual CV's ($\overline{CV}$) are given in Table 7 for each species. The results for NO_2^-, NO_3^-, and SO_4^{2-} show $\overline{CV}$'s of 5.1 percent or less. The corresponding value for NH_4^+ is relatively high at 17 percent.

The individual data were ordered by mean concentration, and average CV's were determined for the upper and lower mean concentration quartiles for each species. The species generally exhibit more relative variability at the low concentrations than at the high concentration. The concentrations marking the lower quartile for each species are identified to give an indication of the distribution of measured concentrations and to show how the precision and absolute concentrations are related in this study.

With the exception of NH_4^+, the precision of replicate analyses is good. The relatively high variability of the ammonium determinations may be due in part to across-day variability of the analytical method as well as sample aging effects. These results suggest that the analytical precision for the determination of each ambient constituent requiring the measurement of NO_2^-, NO_3^-, and SO_4^{2-} is good. Results involving the measurement of NH_4^+ are more variable.

Laboratory Intercomparisons

Several samples were interchanged and analyzed by multiple laboratories. A series of TEA-coated NO_2-spiked filters was provided to RTI by McClenny of EPA. The filters were extracted in 15 ml of DI water and analyzed for nitrite by IC. Results are shown in Table 8. The agreement between the theoretical and measured loadings is good. The average recovery is 101 percent, and the average difference is 0.05 µg NO_2^-.

TABLE 8. COMPARISON OF NITROGEN DIOXIDE-SPIKED SAMPLES

Sample	RTI Analysis[a] µg NO_2^-/ml	Blank-Corrected[b] NO_2^- mass, µg	Theoretical[c] µg	Recovery Percent	Difference µg
9A	0.363	4.76	4.80	99	0.04
9B	0.049	0	--	--	--
14A	0.455	6.14	6.35	97	0.21
14B	0.047	0	--	--	--
17A	0.159	1.70	1.60	106	-0.10
17B	--	--	--	--	--
Blank A	--	--	--	--	--
Blank B	0.043	0	--	--	--

[a] Extraction volume 15 ml.

[b] Mean blank 0.046 µg/ml or 0.69 µg per sample.

[c] Based on loading information provided by EPA (McClenny).

Two KOH bubbler solutions that were used to determine the nitric acid emission rate from the Environment Canada permeation source were analyzed for nitrate by Northrop (Williams) and given to RTI for reanalysis. The results of the Northrop and RTI analyses of Sample No. 2 are 1.28 and 1.19 μg/ml, and 1.11 and 1.06 μg/ml for Sample No. 8. These results show an average difference of 0.07 μg/ml between the results of the two laboratories, with RTI's results 6 percent less than those of EPA.

Eight vials containing nitrate and sulfate QA samples were prepared and provided to RTI by Ellestad of EPA. An extraction volume of 20 ml DI water was added to each vial, and the resulting solution was analyzed for nitrate and sulfate by IC. Results are shown in Table 9. The agreement between the theoretical and measured values is good. The average recovery for nitrate is 99 percent, and the average differences are 0.015 μg at the low concentration and 0.17 μg at the high concentration. The average recovery for sulfate is 99 percent, and the average differences are -0.008 μg at the low concentration and 0.25 μg at the high concentration.

One ADS set and one TFR set of samples from the study initially analyzed by RTI were selected for reanalysis in the EPA (ASB/MDAD/EMSL) laboratories. For each data pair, a mean, standard deviation, and coefficient of variation were computed. The results shown in Table 10 summarize these findings by providing the mean of the individual CV's, the number of pairs considered, and a qualitative indication of whether the second measurement exceeded the first. Comparisons were made only for those cases where both paired data points were above the EPA laboratories' lowest detectable concentration of 0.15 μg/ml.

The results indicate good interlaboratory agreement for NO_2^-, NO_3^-, SO_4^{2-}, and pH, with $\overline{CV}$'s ranging from 1.1 to 14.5 percent. The NH_4^+ reanalysis yielded a $\overline{CV}$ of 33.7 percent for three samples. RTI determines NH_4^+ by colorimetric techniques, while EPA used an ion specific electrode.

TABLE 9. COMPARISON OF ANALYSIS OF NITRATE AND SULFATE QA SAMPLES PREPARED BY EPA (Ellestad)

Sample	Nitrate (μg/Sample)		Recovery Percent	Difference μg	Sulfate (μg/Sample)		Recovery Percent	Difference μg
	Theoretical	RTI Analysis			Theoretical	RTI		
L1	3.02	2.97	98	0.05	3.04	3.35	110	-0.31
L2	1.01	1.04	103	-0.03	1.01	0.96	95	0.05
L3	0.80	0.81	101	-0.01	1.02	1.06	104	-0.04
L4	2.39	2.34	98	0.05	3.05	2.78	91	0.27
H1	10.10	10.00	99	0.10	10.15	10.19	100	-0.04
H2	30.27	29.05	96	1.15	30.40	29.25	96	1.15
H3	23.90	23.50	98	0.40	30.50	30.84	101	-0.34
H4	7.96	7.79	98	0.17	10.20	9.96	98	0.24

TABLE 10. INTERLABORATORY COMPARISONS OF FIELD SAMPLES

Species Comparison	NO_2^-	NO_3^-	SO_4^{2-}	NH_4^+	pH
RTI vs. EPA1[a]					
$\overline{CV}$[b]	8.90	14.52	6.87	33.68	1.10
n	4	8	6	3	3
2nd > 1st?	--	yes	yes	yes	--
RTI vs. EPA2[c]					
$\overline{CV}$		4.60	4.19		
n		5	3		
2nd > 1st?		yes	yes		

[a] EPA1 results are from Loseke (ASB/MDAD/EMSL).

[b] Percent.

[c] EPA2 results are from Ellestad (ARB/APCD/ASRL).

Five samples out of the reanalysis group were analyzed a third time by a different EPA laboratory (Ellestad). Comparison of these values indicates good agreement with RTI; the $\overline{CV}$ is 4.6 percent for NO_3^- and 4.2 percent for SO_4^{2-}. Statistical analysis of the analytical results of the field samples using a t test does not indicate any significant differences between the RTI and either EPA laboratory at the 99 percent confidence level.

Samples were stored for at least a month between the initial analysis by RTI and the second analysis. Uptake of NO_3^-, SO_4^{2-}, and NH_4^+ during storage may account for the results of the second analysis exceeding those of the first in many cases.

Overall, the interlaboratory comparisons show good agreement for each species except ammonium. The results generally agree to within 15 percent or less. There is evidence of aging influences as indicated by the results of the second analysis exceeding those of the first for NO_3^-, SO_4^{2-}, and NH_4^+.

Blank Results

Results of field blanks are summarized in Table 11. The average and standard deviation of the mass found upon extracting and analyzing each sampler component are tabulated. Field blanks were run in the usual manner: sampler components were prepared, assembled, taken to the field site, connected to the flow module with zero flow rate for one sampling period, and returned to the laboratory for disassembly, extraction, and analysis.

The blank results given in Table 12 were used with the appropriate sampled air volumes and data reduction equations to compute equivalent atmospheric concentrations (EAC's). The sampled air volume depends on the sampler employed and, in the case of the TFR, on the component under consideration. As illustrated in Table 12, EAC's for the ADS are generally less than 0.1 $\mu g/m^3$ (~ 0.05 ppb). It should be noted that although the same calculation was performed for NO_2^-, NO_3^-, and SO_4^{2-} from

TABLE 11. BLANK RESULTS

Sampler Component	Species	n	Mass(μg)	SD(μg)
Cyclone	NO_2^-	8	0.183	0.253
	NO_3^-	6	0.983	0.664
	SO_4^{2-}	7	1.540	0.736
	NH_4^+	6	0.600	0.938
Denuder	NO_2^-	12	0.638	0.465
	NO_3^-	8	0.305	0.567
	SO_4^{2-}	12	1.183	1.166
	NH_4^+	5	3.120	0.965
Teflon Filter	NO_2^-	10	1.172	1.182
	NO_3^-	10	0.426	0.467
	SO_4^{2-}	10	0.212	0.463
	NH_4^+	8	0.920	0.818
Nylon Filter	NO_2^-	6	0.520	0.634
	NO_3^-	10	0.234	0.498
	SO_4^{2-}	6	0.796	0.926
Nylon Strip	NO_3^-	9	0.045[a]	0.133[a]
Naphion Strip	NH_4^+	5	3.160	0.439
Oxalic Acid Filter	NH_4^+	4	1.987	1.497
TEA Filter	NO_2^-	8	1.185	0.298
	NO_3^-	10	0.538	0.552
	SO_4^{2-}	8	1.513	0.786

---

[a] Other results in our laboratory suggest the tabulated values may be low. Ellestad (ARB/APCD/ASRL) reports 0.32±0.02 μg.

TABLE 12. SUMMARY OF ESTIMATED EAC's AND DL's FOR DAILY OPERATION OF THE ADS AND TFR SAMPLERS

Species	EAC[a] (µg/m^3)		DL(a)[b] (µg/m^3)		DL(b)[c] (µg/m^3)	
	ADS	TFR	ADS	TFR	ADS	TFR
HONO (as NO_2^-)	0.034	--	0.054	--	0.107	--
HNO_3 (as NO_3^-)	0.016	0.025[d]	0.054	0.558	0.130	0.247
SO_2 (as SO_4^{2-})	0.064	0.720	0.054	0.476	0.267	1.843(2)
NO_2	--	0.564	--	0.476	--	0.990
NH_3 (as NH_4^+)	0.169	0.881	0.054	0.139	0.325(1)	1.248(25)
NO_3^- (on nylon)	0.013	0.011	0.054	0.047	0.094(3)	0.082
NO_3^- (on Teflon)	0.023	0.020	0.054	0.047	0.099(8)	0.086(7)
SO_4^{2-}	0.011	0.010	0.054	0.047	0.086	0.076
NH_4^+ (on Teflon)	0.050	0.044	0.054	0.047	0.183	0.160
NH_4^+ (on oxalic acid filter)	--	0.094	--	0.036	--	0.307(3)

---

[a] EAC = equivalent atmospheric concentration computed from blank value and sampled air volume.

[b] DL(a) = detection level computed from analytical detection level of 0.05 µg/mL.

[c] DL(b) = detection level computed from blank, variability of blank, and sampled air volume.

[d] Other results in our laboratory suggest the tabulated value may be low. An EAC based on Ellestad's results is 0.178 µg/m^3.

[e] The entry contained within parentheses represents the number of cases where data in the current daily study failed to exceed the tabulated DL.

the first two denuders, the tabulated results in these cases represent upper bounds. This is because in the actual computations for HONO, HNO_3, and SO_2, the second denuder species loading is subtracted from the first making the blank correction automatic.

Except for SO_2, NO_2, and NH_3, EAC's for the TFR are similar to those for the ADS. TFR EAC's for SO_2, NO_2, and NH_3 are 0.720, 0.564, and 0.881 $\mu g/m^3$ (0.2, 0.3, and 1.1 ppb).

All the data reported in the current study with the exception of hydrogen ion data (H^+) have been corrected for blanks. EAC's for ADS and TFRs are 4.6 and 4.0 n mol/m^3.

Detection levels can be estimated in several ways. One method uses the analytical detection level to estimate the corresponding atmospheric concentration. A second method uses the field blank and the variability of the field blank to make a similar estimate. Both of these methods were employed in the current study. Respective results, designated as DL(a) and DL(b), are presented in Table 12.

The DL(a) values are based on an analytical detection level of 0.05 $\mu g/mL$ for NO_2^-, NO_3^-, SO_4^{2-}, and NH_4^+. In most cases for both the ADS and TFR, the tabulated results are less than 0.1 $\mu g/m^3$ (~ 0.05 ppb). Exceptions are TFR, HNO_3, SO_2, NO_2, and NH_3 with DL(s)'s of 0.558, 0.476, 0.476, and 0.139 $\mu g/m^3$ (0.2, 0.1, 0.2, and 0.2 ppb).

Based on the blank and variability of the blank results, detection levels (DL(b)) were estimated for each species. The sum of the blank and three times the standard deviation of the blank were normally used along with the appropriate sampled air volumes and data reduction equations to compute DL(b)'s. Only the blank standard deviations were used for ADS HONO, HNO_3, and SO_2, since in these cases, blank correction is automatic.

As illustrated in Table 12, DL(b)'s for the ADS are generally less than 0.3 $\mu g/m^3$ (~ 0.15 ppb). Ammonia is an exception, with a DL(b) of 0.325 $\mu g/m^3$ (0.4 ppb). With three exceptions, SO_2, NO_2, and NH_3, DL(b)'s for the TFR and ADS show similar behavior. TFR DL(b)'s for SO_2, NO_2, and NH_3 are 1.843, 0.990, and 1.248 $\mu g/m^3$ (0.4, 0.5, and 1.6 ppb).

Individual daily data in the current study were compared with the tabulated DL's. Few cases were noted where the reported concentration fails to exceed the estimated DL. One notable exception is with the TFR NH_3 where the DL(b) was exceeded in only one of 26 cases.

Volumetric Flow Measurement

Volumetric flow rates were measured at the start and at the end of each experiment for each sampler using a dry gas meter (DGM). In addition, measurements for the weekly samples collected during the intensive study were performed daily. These flow rates were corrected for temperature and pressure effects and adjusted to standard conditions (STP) of 0°C and 760 torr.

Flow rate determinations were made using the RTI DGM and flow meters employed by other participating groups to permit intercomparison of resulting concentration data. Comparison of flow rates determined with the RTI DGM and the DGM used by Ellestad agreed to within 2.3 percent.

The set points on all flow control units (both ADS and TFR) were not changed during the experiment. Averages and standard deviations of flow rates are shown in Table 13. The average flow rates agree well within systems. With the exception of ADS module number 4, the variation (as expressed by standard deviation) at the nominal 14 SLPM flow rate is small. This level of precision does not differ appreciably from that of the DGM.

ADS pump module 4 has significantly greater variation than the other ADS pump modules, indicating its poorer regulation (an F test shows a significant difference with a probability exceeding 99 percent). As a result, the precision of ADS concentration determinations was examined to see if an effect of flow variation resulting from pump module 4 is apparent. The precision of the difference of daily SO_2 and fine particle SO_4^{2-} concentration determinations observed using pump

TABLE 13. FLOW RATES FOR ADS AND TFR SAMPLERS
DURING THE INTENSIVE MEASUREMENT PERIOD
(SLPM at 0°C, 760 Torr)

	ADS Module			
	1	2	3	4
Average	13.97	14.12	13.87	14.07
Standard Deviation	0.32	0.30	0.50	1.88
CV[a]	2.3	2.1	3.6	13.4

	TFR				
	TEA Filter		High Volume		Cyclone Bleed
MFC No.	1	2	3	4	5
Average	1.65	1.58	14.38	14.18	1.05
Standard Deviation	0.10	0.10	0.25	0.26	0.05
CV	6.2	6.4	1.7	1.9	4.7

	TFR Total[b]	
MFC No.	1 and 3	2 and 4
Average	16.03	15.75
Standard Deviation	0.27	0.28
CV	1.7	1.8

---

[a] Percent.

[b] This is the flow across the Nafion and nylon strips and is the sum of TEA filter and high volume flows.

modules 1 and 2 was compared with that observed using pump modules 3 and 4. The species SO_2 and fine particle SO_4^{2-} were chosen since they should not experience interconversion or volatilization, which could obscure flow variation effects. No significant difference was found for the two sets of measurements.

The higher CV's seen on the TEA filter and cyclone bleed flow rates are due largely to the use of MFCs designed to regulate at approximately three to five times the flow rates actually used. Reducing the range of the flow controllers employed should improve the control sensitivity and the precision of the resulting flow rates.

QC Check for TFR Nitric Acid Concentration

The ratio of nitrate found on the nylon strip to the sum of that found on the nylon strip, Teflon filter, and the nylon filter was calculated for each TFR sample. Based on the published protocol for using the TFR, this ratio should be less than or equal to 0.085. As a result, inspection of this ratio represents a quality control check of the TFR results for nitric acid. For the two nitric acid spiking experiments, the ratios were 0.133 and 0.114. For the 26 daily samples, this ratio averaged 0.122 ± 0.029 and in 21 cases exceeded 0.10. Since the QC checks for HNO3 exceeded 0.085 in most cases, and since the calculation of TFR Fine NO_3^- depends on the HNO_3 results, the resulting TFR Fine NO_3^- were in error. In 24 of 26 cases, the TFR Fine NO_3^- are negative. These findings suggest that the TFR HNO_3 and Fine NO_3^- results in the current study are suspect.

The individual components comprising each TFR were identified and recorded. The HNO3 QC ratios (nitrate on the nylon strip to the sum of nitrate on the strip, Teflon filter, and nylon filter) were examined for possible association with each of the four TFR tubes used. At the 95 percent confidence level, an F-test does not indicate differences across tubes. This means that the high QC ratios noted above are not associated with differences in the tubes holding the nylon strips in the TFR.

Following each sampling period, the TFR was disassembled and inspected. On six occasions, the nylon strip had separated from the tube wall. The QC ratios in these cases do not appear to be outliers when compared with those where visual inspection revealed no anomalies.

SPECIAL STUDIES

Data collected during the course of the overall study was used to address several issues. These topics range from various operational and performance characteristics of individual samplers to comprehensive comparison of results. These topics are termed "Special Studies" and are described in the following subsections.

Nitric Acid Spiking Experiments

Two sets of experiments were performed where ambient air spiked with nitric acid was sampled. These spiking experiments were conducted just prior to the beginning and just after the termination of the intensive sampling period. The first experiment was conducted on 9/26/86 and the second on 10/12/86. Nitric acid used in these experiments was supplied from permeation source provided by the Environment Canada group.

In the first experiment, two tests were performed where nitric acid was delivered for approximately 10 minutes to bubblers containing aqueous solutions of KOH. These were analyzed for NO_3^- by IC (Williams, Northrop) to determine the nitric acid spiking rate. For the next 144 minutes, one ADS sampled ambient air containing 8.8 $\mu g/m^3$ HNO_3 as determined by the Unisearch laser system. For one hour of that period, nitric acid was introduced from the source directly into the ADS cyclone inlet through a 1/8" OD Teflon line. At the end of the sampling period, duplicate determinations of the nitric acid emission rate were made. A pair of TFR samplers was used with a common cyclone to sample ambient air containing 6.5 $\mu g/m^3$ of nitric acid for the next 210 minutes. For two hours of that period, nitric acid was added from the source as described above. At the end of the sampling period, the nitric acid emission rate was measured again in duplicate.

The second experiment was conducted in a manner similar to the first. The following differences should be noted: another spiking test with an ADS was performed after the TFR test, the sampling and spiking durations were the same, the background level of nitric acid as determined by Unisearch was only 0.87 $\mu g/m^3$, and additional duplicate nitric acid emission rate determinations were made.

The ADS and TFR were operated by RTI, and the constituent parts were extracted and analyzed in the RTI laboratory. The ambient concentrations of a conservative species, sulfate, were determined with the ADS and TFR and compared for each experiment. The resulting good agreement suggests that, on the basis of flow rates, both systems were operating properly.

Results from the spiking experiments are shown in Table 14. Measured nitric acid emission rates are shown for each experiment and were approximately 1.15 µg/min. The background-corrected emission rates as determined by the ADS and TFR are shown based on three estimation methods. The first method assumes that the sum of the nitrate collected on the components of each sampler was nitric acid and is labeled "Total." The next method employs the individual method protocol for determining nitric acid for that sampler, including the nitrate contribution from the cyclone that is assumed to be retained nitric acid; it is labeled "HNO_3 with Cyc." The third method repeats the previous method but ignores the contribution of the cyclone and is labeled "HNO_3 without Cyc."

The tabulated results show good agreement between the measured emission rates and those determined using total nitrate recovered from ADS and TFR. There is also good agreement between the measured emission rates and "HNO_3 with Cyc" for the three ADS tests. The agreement is not as good for the TFR, where the "HNO_3 with Cyc" exceeds the measured emission rates. For the two paired TFR tests, the ratios of nitrate on the nylon strip to the total on the nylon strip, Teflon filter, and the nylon filter were determined. These values, 0.133 and 0.114, exceed the method protocol calculation factor of 0.085 and account for the overestimates of nitric acid by the TFR.

TABLE 14. RESULTS OF NITRIC ACID SPIKING EXPERIMENTS

Sampler	Date 1986	Sampler-Determined Emission Rate (μg/min) Total	HNO$_3$ with Cyc	HNO$_3$ without Cyc	Measured Emission Rate	Cyc Recovery[a]
ADS	9/26	1.25	1.15	1.00	1.16 ± 0.05	9.6
TFR	9/26	1.00	1.73	1.64	1.16 ± 0.05	6.1
ADS	10/12	1.12	1.09	0.96	1.14 ± 0.11	13.8
TFR	10/12	1.07[b]	1.29	1.16	1.14 ± 0.11	12.1
ADS	10/12	1.20	1.10	0.99	1.14 ± 0.11	10.3

[a] Percent of total nitrate found in the cyclone extract.

[b] Includes a 9 percent contribution found in the extract of the filter pack.

Comparison of the emission rates determined with and without accounting for the nitric acid retention by the cyclone shows an appreciable difference. For these tests, approximately 10.4 ± 2.9 percent of the recovered nitrate was found on the cyclone. This provides a strong argument for incorporating nitrate from the cyclone extract analysis in the use of either the ADS or TFR in their current configurations.

Interaction of Nitric Acid in Cyclones

Experiments were performed to study the absorption and recovery of nitric acid from Teflon and Teflon-coated cyclones. Three cylones were tested: an EPA-style cyclone made of TFE Teflon, an FEP Teflon-coated aluminum cyclone, and an Italian cyclone made of TFE Teflon. All cyclones were cleaned prior to testing. They were first sonicated for 30 minutes in deionized water and then vacuum-dried at 80°C for 1.5 hours. The concentration of nitric acid was measured before, during, and after the cyclone was connected in-line using the Environment Canada TDLAS. Environment Canada also provided the nitric acid source, a diffusion tube with a nominal emission rate of 1.15 ± 0.10 μg/min. Total flow through each cyclone was 14.4 SLPM. Thus, the nominal nitric acid concentration delivered to each cylone was 80 $\mu g/m^3$ (28 ppb).

Nitric acid transmission values, determined as the ratios of nitric acid measured downstream to that measured upstream of the cyclone are displayed as a function of exposure time in Figures 3 to 5. For the EPA-style cyclone, as used with the ADS, the nitric acid transmission approaches 1.0 after approximately 15 minutes. For the Teflon- coated aluminum cyclone, the value approaches 1.0 in less than 10 minutes. For the Italian cyclone that was used with one of the ADS systems in the 1985 LA study, the transmission approaches a steady value after approximately 15 minutes but displays a value of 0.9 rather than 1.0, as found with the other two cyclones.

The one standard deviation error bars for three points are displayed along with the results from each test in Figures 3 to 5. These error bars show the minimum and maximum values for nitric acid transmission due to the accuracy and drift of the nitric acid concentration measured by the TDLAS.

Results from several nitric acid absorption and recovery experiments are summarized in Table 15. Based on the total µg of nitrate determined by IC analysis of deionized water cyclone extracts, the nitrate recoveries for the three cyclones examined in the current study range from 8 to 23 percent. Results are included from five other tests where nitric acid vapor from the same source was used to spike ADS or TFR samples. These five tests had an average recovery of 9.2 ± 4.1 percent.

These results show that an appreciable amount of nitric acid may be retained by Teflon cyclones, and that the transmission of nitric acid approaches 100 percent after a brief conditioning period. The nitric acid transmission properties of Teflon, however, may be dependent on undefined properties of the Teflon itself. This is illustrated by the difference in nitric acid transmission displayed by the cyclone made of domestic TFE Teflon and that made of Italian TFE Teflon.

Cyclone Bleed Filter

A Na_2CO_3-coated Gelman A/E glass fiber filter was placed in the bleed stream that was drawn from the base of the TFR cyclone. The volumetric flow rate of the bleed stream was nominally 1.0 SLPM. This amounts to 3.2 percent of the total flow through the TFR. The coated filter was extracted and analyzed to determine the contribution of the bleed to the total gaseous and particulate nitrate (Total NO_3^-) and the total gaseous and particulate sulfate (Total $SO_2+SO_4^{2-}$) recovered from the TFR. On the average, 3.8 ± 1.4 percent of the Total NO_3^- and 3.8 ± 0.7 percent of the Total $SO_2+SO_4^{2-}$ were recovered from the bleed stream. This 3.8 percent contribution compares favorably to the 3.2 percent

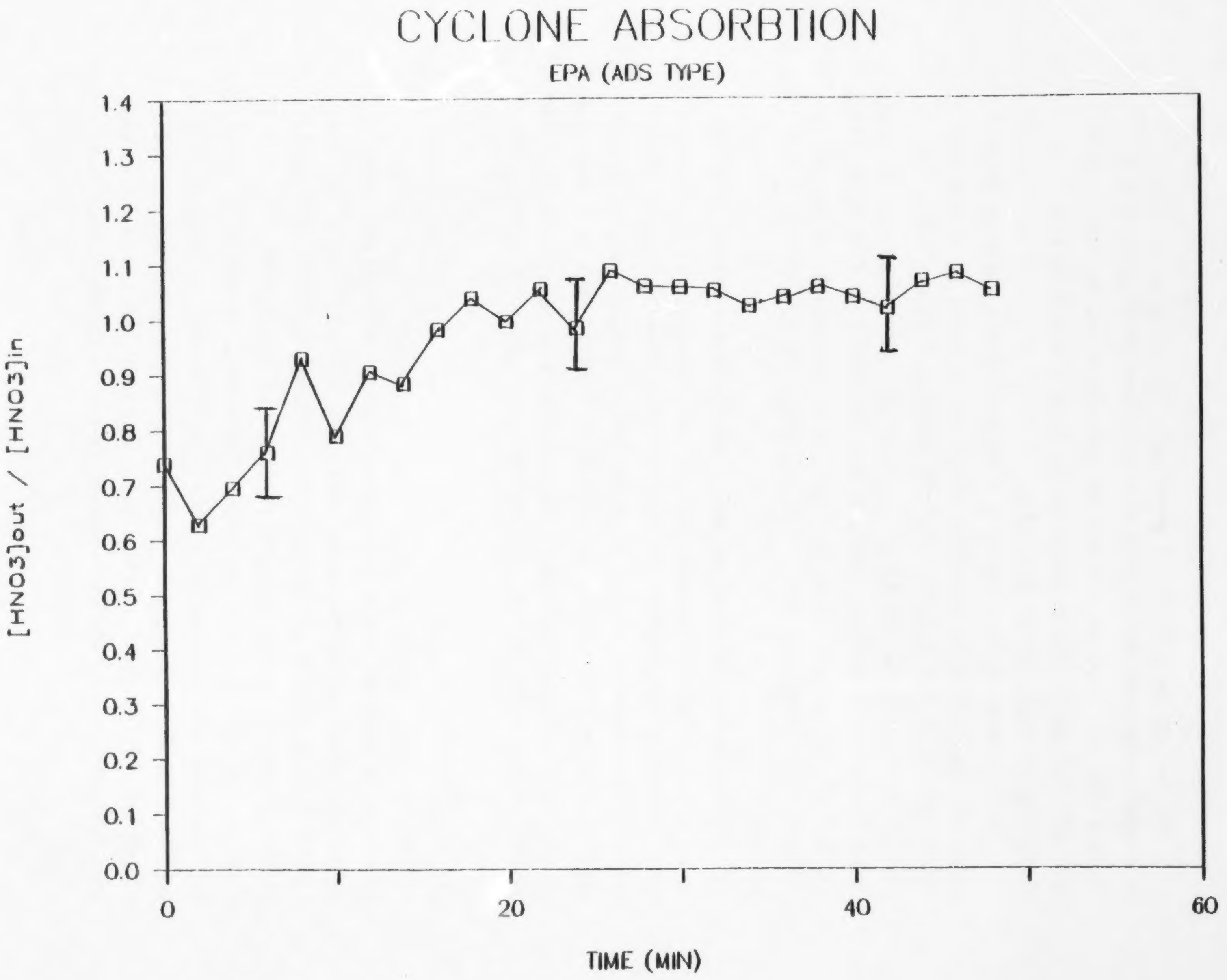


Figure 3. Nitric acid transmission for the EPA style TFE cyclone.

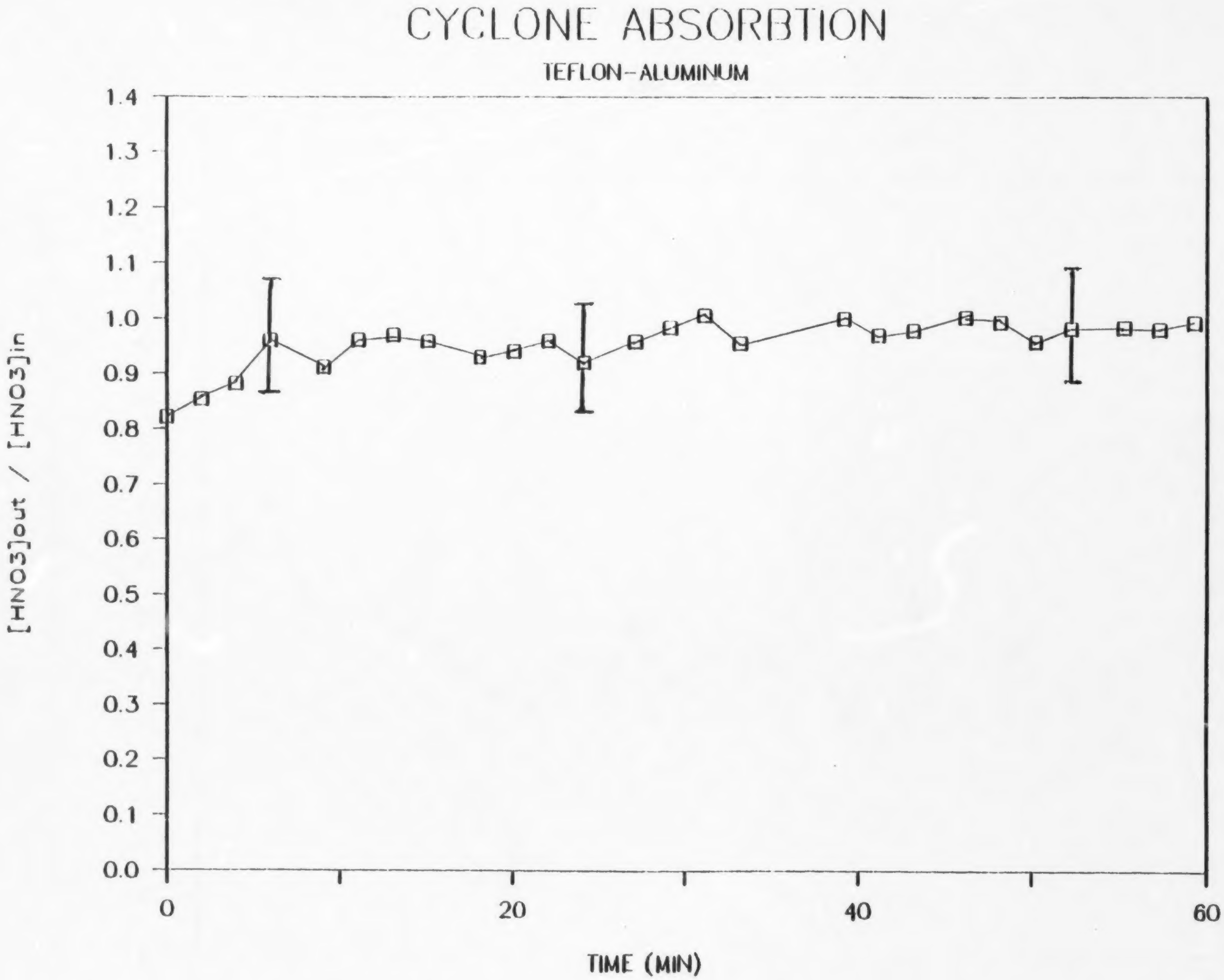


Figure 4. Nitric acid transmission for the FEP Teflon-coated aluminum cyclone.

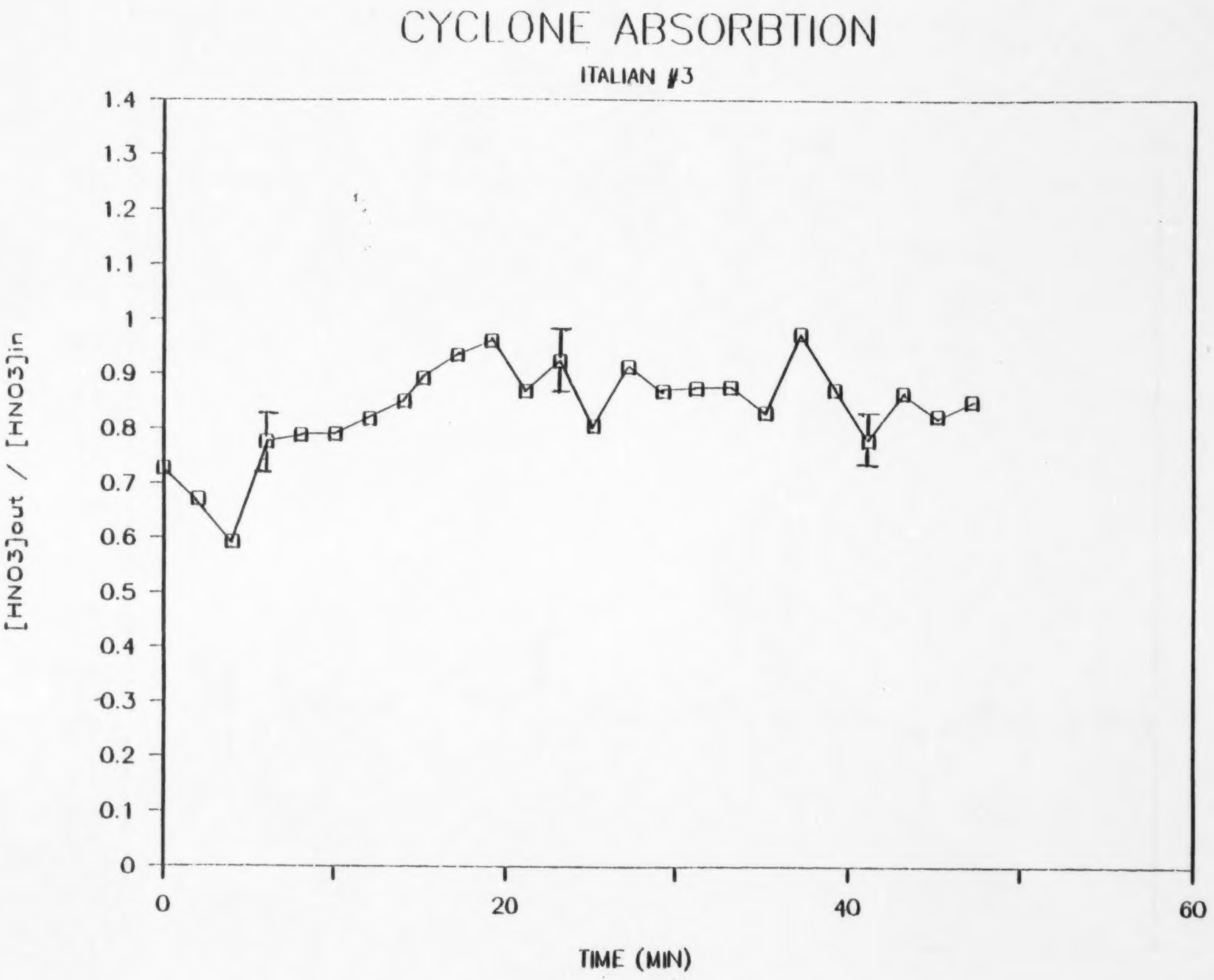


Figure 5. Nitric acid transmission for the TFE Italian cyclone.

TABLE 15. RESULTS OF NITRIC ACID ABSORPTION AND RECOVERY TESTS WITH CYCLONES

Sample I.D.	Test Duration Minutes	Flow Rate SLPM	µg HNO_3 Delivered from Diffusion Tube	µg NO_3^- Recovered	Recovery Percent
EPA (ADS type)	48	15.6	55.2	5.86	10.6
Teflon-Aluminum	242	15.5	278.3	21.08	7.6
Italian No. 3	50	15.5	57.5	12.98	22.6
ADS 1 HNO_3 spike 1	144	14.0	165.6	8.98	5.4
TFR HNO_3 spike 1	210	32.6	241.5	10.36	4.3
ADS 3 HNO_3 spike 2	60	14.2	68.4	9.42	13.8
ADS 4 HNO_3 spike 2	60	14.2	68.4	7.54	11.0
TFR HNO_3 spike 2	120	31.1	138.0	15.54	11.3

[a] Percent recovered = $\frac{\mu g\ NO_3^-\ \text{recovered}}{\mu g\ \text{delivered from diffusion tube}}$ (100)

volumetric contribution noted above. This agreement indicates that in the daily samples of the current study, the bleed stream was not needed to remove collected large particulate sulfate and nitrates from the TFR cyclone. It also means that corrections to account for constituent losses in the bleed stream are small.

Cyclone Performance

Cyclones of identical design were employed with the ADS and the TFR. Since the volumetric flow rate used in the ADS (e.g., 14 SLPM) differed appreciably from that in the paired TFR (e.g., 33 SLPM), the particle collection efficiencies were also different. At the two flowrates, the D_{50} ($\rho = 1.0$) cut sizes for the ADS and TFR are estimated to be 3.3 and 1.8 µm, respectively. As a result, the nitrate and sulfate loadings were higher in the TFR cyclone than the ADS cyclone. During the 13-day study, the average nitrate and sulfate concentrations based on loadings in the TFR cyclone exceeded the corresponding values for the ADS cyclone by 44 and 35 percent. This is illustrated in Figures 6 and 7.

The nitrate retained in the cyclone can comprise a substantial fraction of the Total NO_3^-. This value typically is 20 to 40 percent but was observed as high as 70 percent on one day. For the 13-day study the nitrate collected in the ADS cyclone represents 59.4 ± 15.6 percent of the total particulate nitrate (i.e., that on the cyclone, the Teflon filter, and the nylon filter). This value should be even higher for the more efficient TFR cyclone and is estimated to be 85.3 percent. The contribution of the cyclone catch is generally smaller for total particulate sulfate and ammonium--typically 10 percent for sulfate and 5 percent for ammonium. Studywide average cyclone catch

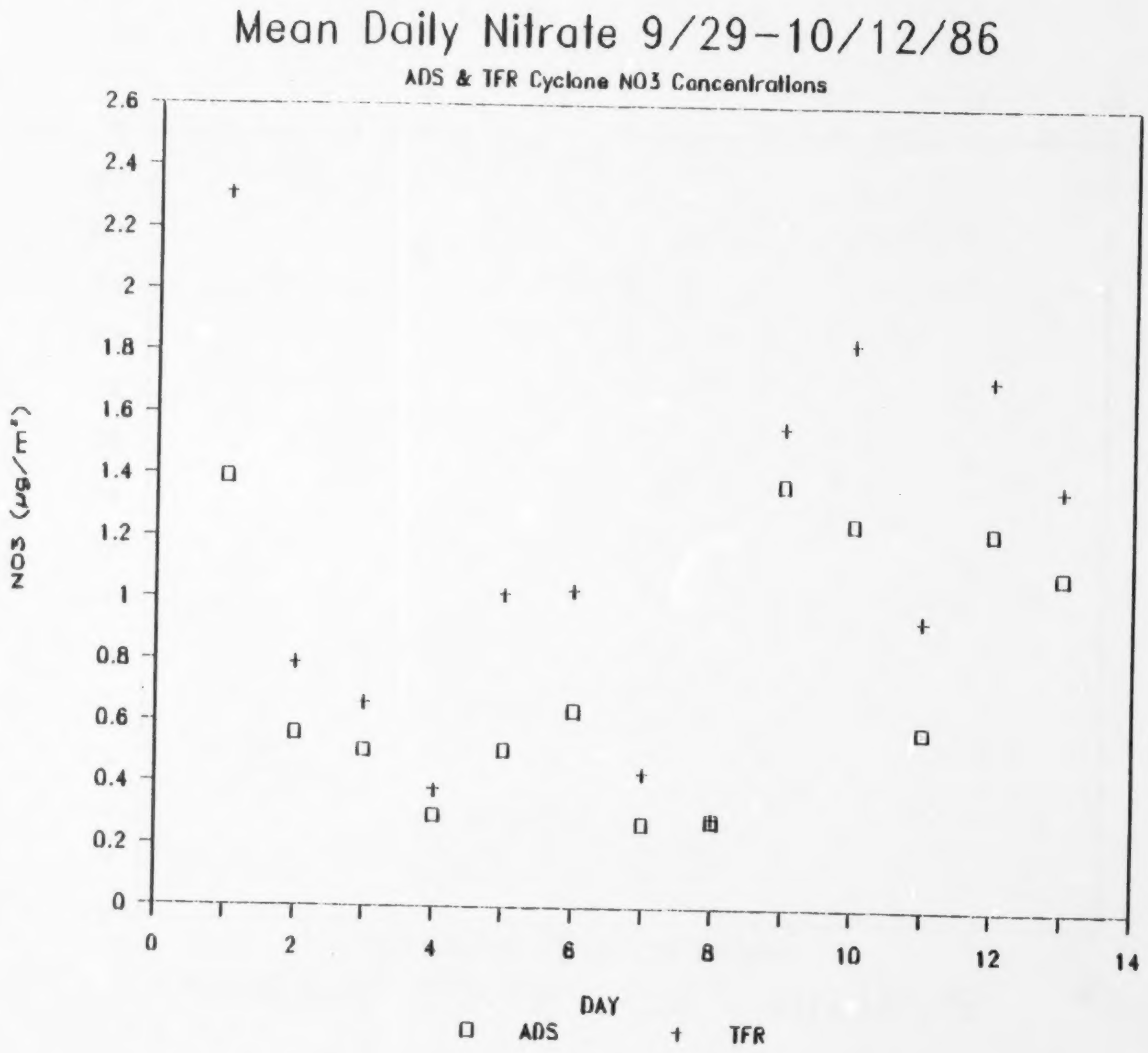


Figure 6. Daily mean nitrate concentrations on ADS and TFR cyclones.

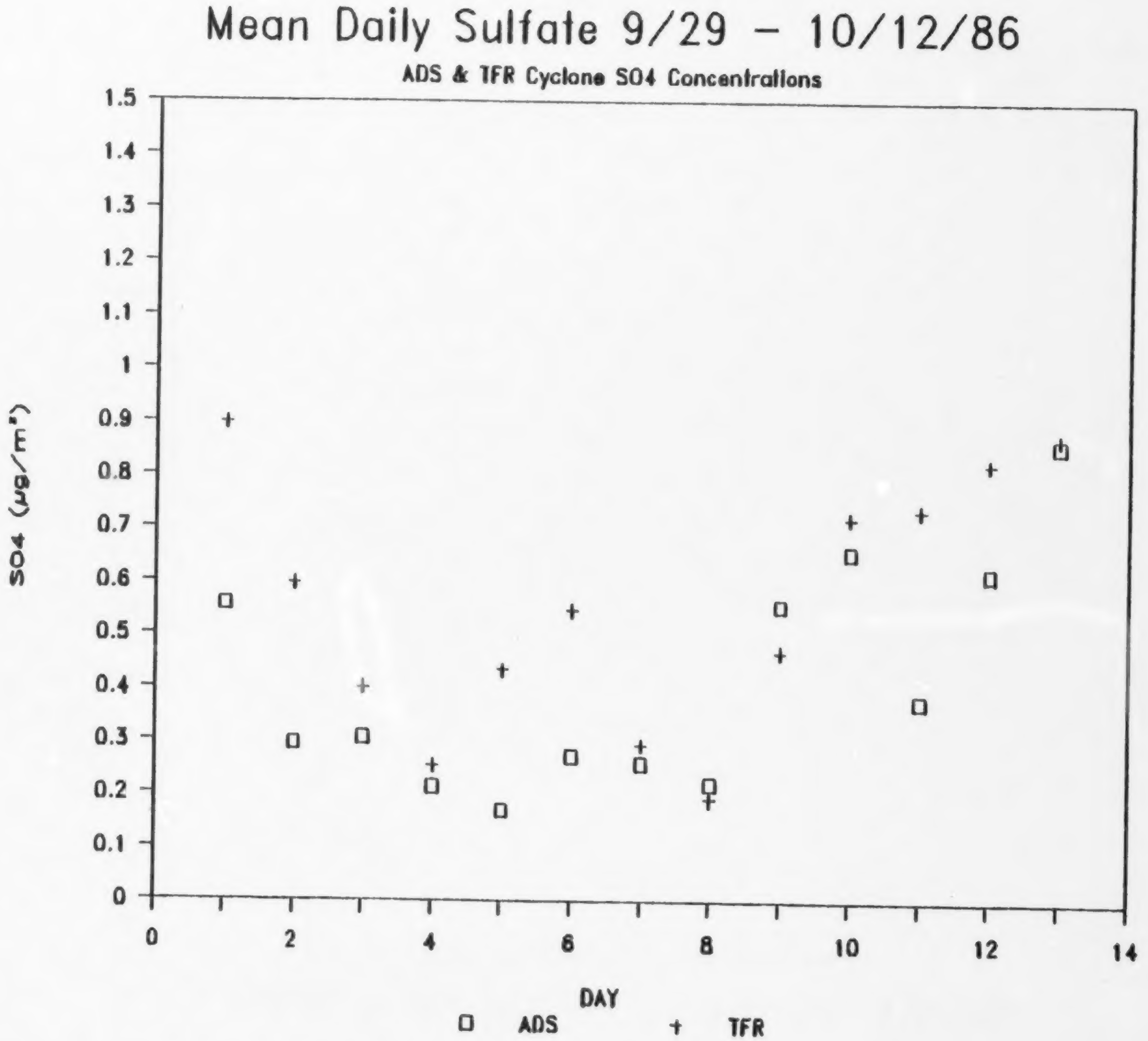


Figure 7. Daily mean sulfate concentrations on ADS and TFR cyclones.

contributions for the TFR and ADS are given in Table 16 and show enhanced collection efficiency for the TFR. The variation in the behavior of the day-to-day profiles illustrated in Figures 8 to 10 show the influence of daily variations in ambient particle size distribution on the contribution of the cyclone catch. These results underscore the importance of considering the difference in particle collection efficiencies of the cyclones in the TFR and ADS when comparing their performance for sampling and analysis of acidic species.

Data were examined to see if the fine particle concentrations determined using the ADS exceed those from the TFR, as expected. The fine particle nitrate (Fine NO_3^-) data could not be compared since the TFR does not resolve this parameter. The fine particle sulfate (Fine SO_4^{2-}) data were examined for the ADS and TFR. Using differences of paired daily mean concentrations, the ADS Fine SO_4^{2-} exceeded that from the TFR by 0.304 ± 0.375 $\mu g/m^3$ or 5.1 percent. Using a t test, this difference is significant at the 95 percent confidence level. Examination of the ammonium data, using a similar test, revealed unexpected results. The ammonium on the TRF Teflon filter exceeded that from the ADS by 0.291 ± 0.115 $\mu g/m^3$, and this difference is significant at the 95 percent confidence level. This unexpected finding may be the result of the ADS undersampling Fine NH_4^+ . This seems unlikely in view of the previously noted comparison of ADS and TFR Fine SO_4^{2-}, although NH_4^+ collected by the ADS may be lost to volatilization. It may result from gaseous NH_3 being retained on the TFR Teflon filter by cocollected acidic species.

Volatilized Fine Nitrate

Examination of the ratio of nitrate on the ADS nylon filter to the sum of nitrate on the Teflon and nylon filters provides a measure of the fraction of Fine NO_3^- that volatilizes after capture. The average of this value for the daily samples is 0.52 ± 0.23, while the average for the weekly samples is 0.93 ± 0.05. This suggests that for longer duration samples a larger fraction of the collected fine nitrate is

TABLE 16. STUDYWIDE AVERAGES OF DAILY CYCLONE CATCH CONTRIBUTIONS FOR TFR and ADS

Species Sum	Contribution[a], %	
	TFR	ADS
Total NO_3^-	34.6 ± 18.0	24.7 ± 13.3
Part. NO_3^-	85.3[b]	59.4 ± 15.6
Total SO_4^{2-}	10.6 ± 9.3	9.1 ± 9.7
Total NH_4^+	6.0 ± 5.6	3.0 ± 5.0

[a] Calculated as mass of indicated species recovered from the the cyclone times 100 divided by the species sum. The Total NO_3^- includes all gas and particulate NO_3^-; the Part. NO_3^- includes all particulate NO_3^-; the Total SO_4^{2-} includes all particulate SO_4^{2-}; and the Total NH_4^+ includes particulate NH_4^+.

[b] Estimated.

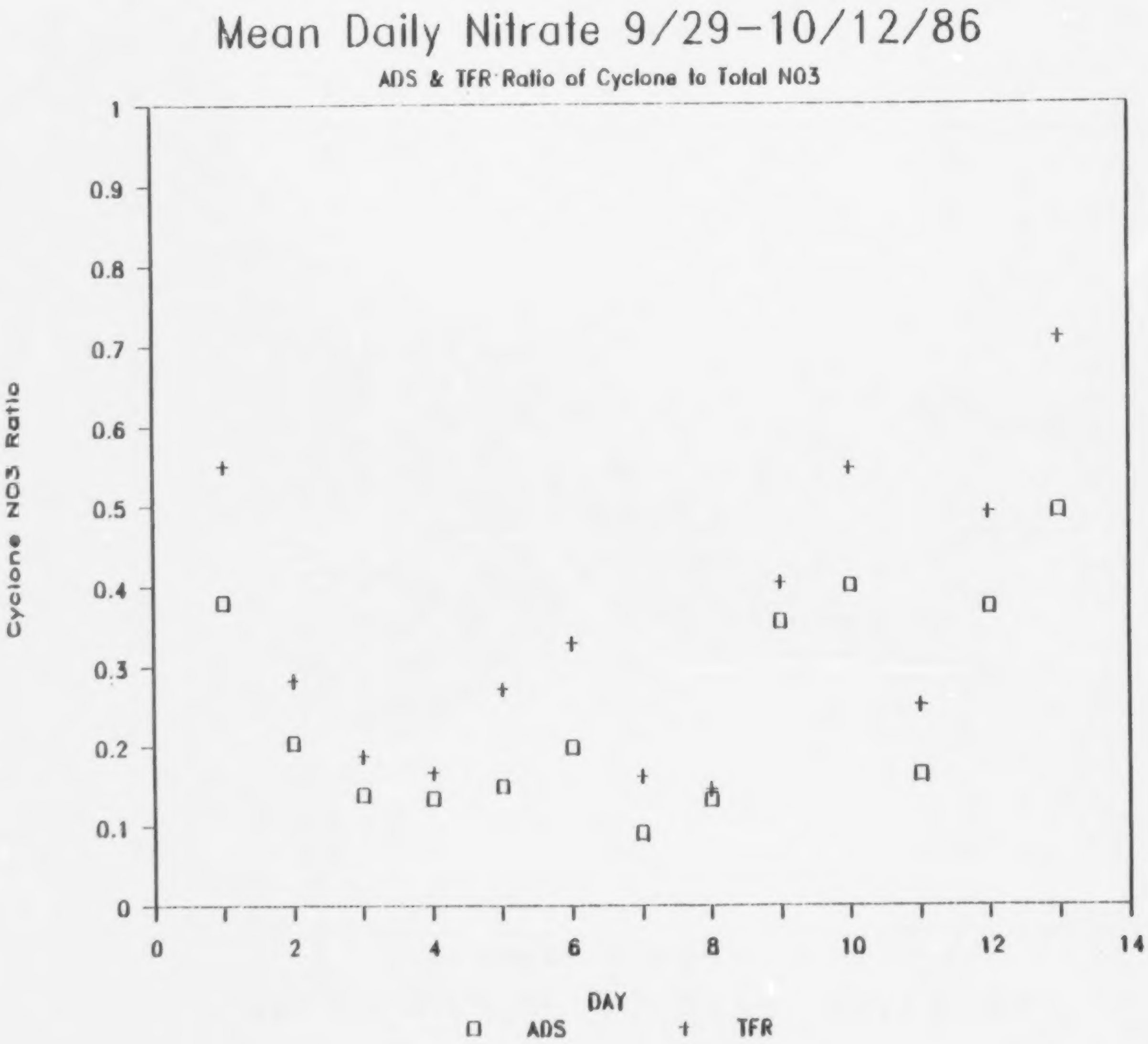


Figure 8. Daily mean ratio of cyclone nitrate to total gaseous and particulate nitrate on ADS and TFR.

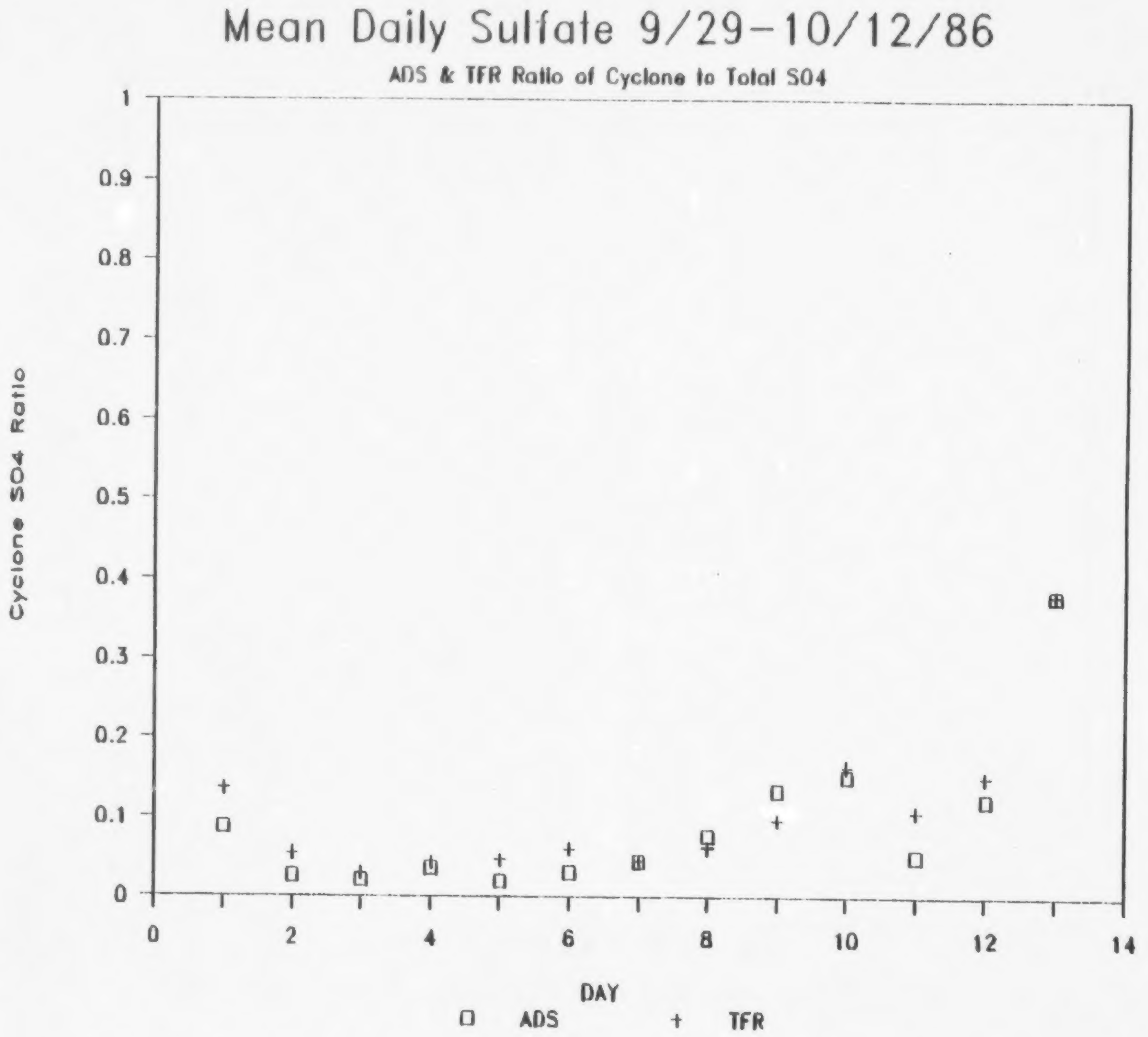


Figure 9. Daily mean ratio of cyclone to total particulate sulfate in ADS and TFR.

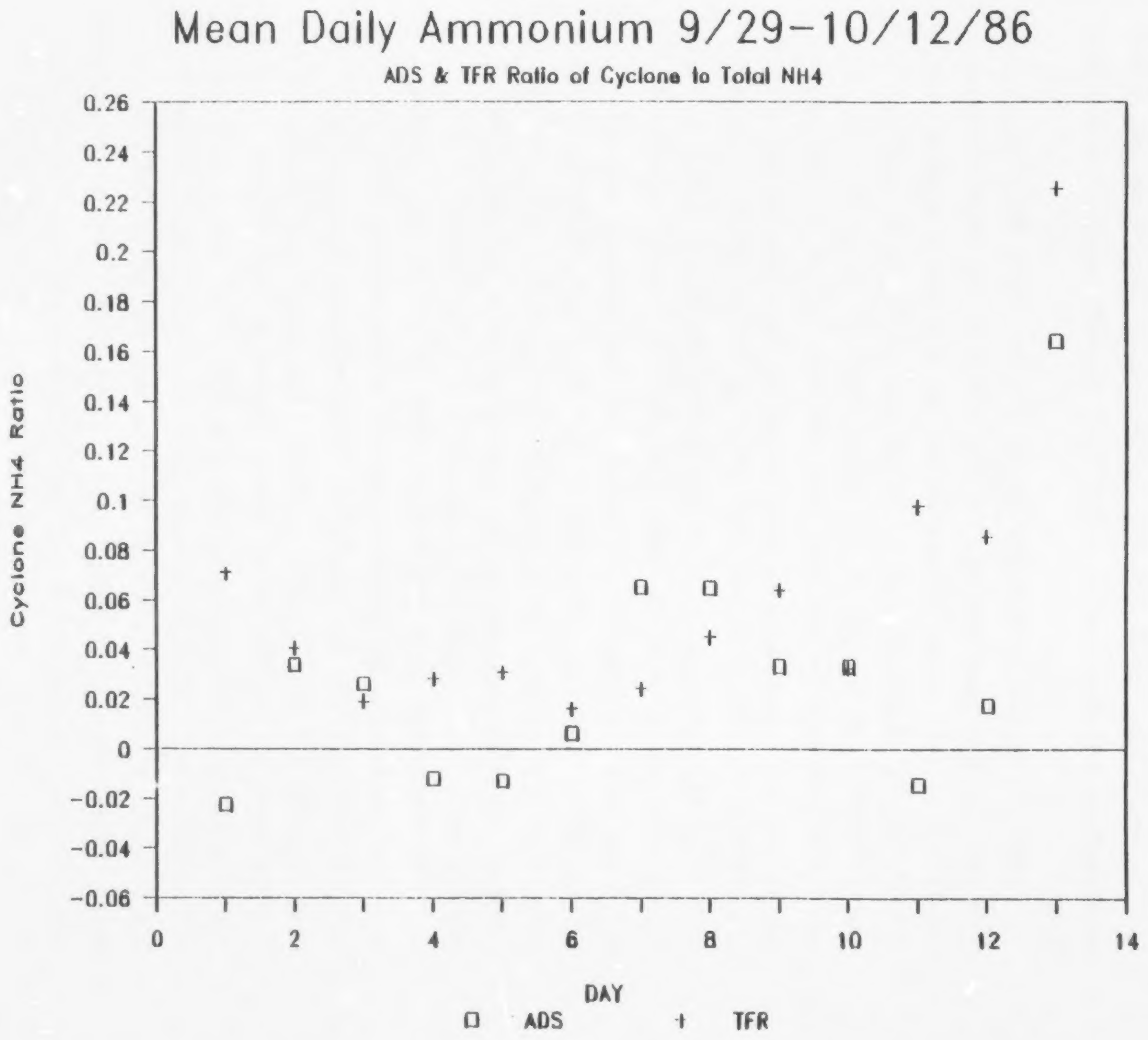


Figure 10. Daily mean ratio of cyclone to total particulate ammonium on ADS and TFR.

lost to volatilization in the ADS. This volatilization may be caused by departure from equilibrium or by reaction with codeposited strong acids.

When the sample reaches the Teflon filter in the ADS, the gaseous HNO_3 and NH_3 have been removed. In the TFR when the sample reaches the Teflon filter, 91 and 83 percent of the originally present HNO_3 and NH_3 should remain airborne. If ambient NH_4NO_3 is in equilibrium with HNO_3 and NH_3 and if its volatilization is sensitive to a departure from equilibrium, then the complete removal of HNO_3 and NH_3 in the ADS should enhance volatilization over that in the TFR. This hypothesis cannot be examined directly with results from the current study for two reasons. The Teflon filters in the ADS and TFR did not receive samples with the same fine particle loading because of the different particle removal efficiencies of the cyclones employed in the two systems. Secondly, since the TFR Teflon filter receives sample containing gaseous HNO_3 and fine particulate nitrate, the original phase of the HNO_3 captured on the downstream nylon filter cannot be reconciled.

The difference in particle collection efficiency can, however, be addressed indirectly by comparing the nitrate recovered from the TFR and ADS cyclones. On the average 0.335 $\mu g/m^3$ more NO_3 was recovered from the TFR than the ADS cyclone. The sum of this value and the nitrate found on the TFR Teflon filter should be less than or equal to the fine particle nitrate found with the ADS (i.e., sum of nitrate on Teflon and nylon filters). If the close approach to equilibrium in the TFR prevents nitrate volatilization, then the two values will be approximately equal. If appreciable nitrate volatilization occurs in the TFR, then the sum of the cyclone difference and the TFR Teflon nitrate will be less than the ADS fine particle nitrate. Results in the current study show the two values to be highly correlated (i.e., $r = 0.93$) with a mean ratio not significantly different from unity. This suggests that on the average in the current study little nitrate is lost from the TFR Teflon filter and that the departure from equilibrium is largely responsible for volatilized fine nitrate in the ADS.

Behavior of Ammonium Nitrate

The TFR employs an oxalic acid-coated filter to collect ammonia passing the Nafion strip as well as any ammonia that is volatilized from ammonium nitrate collected on the Teflon filter. The ADS in the configuration used in most cases of the current study for daily sampling did not employ a collection medium for volatilized particulate ammonium. The rationale for this approach is that the ammonia that is subject to volatilization is hypothetically retained as a salt by cocollected acidic constituents. Data collected in the current study can be employed to address this issue.

Data for the total nitrogen determined as ammonium (Total $NH_3+NH_4^+$) were examined. The studywide mean values for the TFR and ADS are 2.911 ± 1.180 and 2.545 ± 1.134 $\mu g/m^3$, respectively. These results suggest that the TFR was collecting more ammonium than the ADS. The differences in the paired determinations were examined for the 13 days of the study. The TFR exceeds the ADS on the average by 0.366 $\mu g/m^3$, and this difference is not zero with 95 percent confidence.

During the last 4 weeks of the 3-month weekly sampling period, citric acid-coated filters were added to the ADS train downstream of the nylon filter. This was done to test for ammonia volatilization from the particulate collected on the Teflon filter. Appreciable ammonium was found, amounting on the average to 0.083 of the Total $NH_3+NH_4^+$. When these weekly results are extrapolated to the previously discussed daily test results, approximately 60 percent of the discrepancy between the ADS and TFR Total $NH_3+NH_4^+$ can be accounted for as unsampled volatilized ammonium. The fate of the remainder is unresolved. It may, however, be collected as NH_3, NH_4^+, or both on the Na_2CO_3-coated denuders or other constituent parts of the ADS that are not extracted and analyzed for ammonium.

The volatilized ammonium in the four weekly ADS samples where data are available was compared to the volatilized NO_3^- found on the nylon filters. On the average, 93 ± 5 percent of the nitrate entering the Teflon filter is apparently volatilized and retained by the nylon filter. If it is assumed that the nitrate recovered from the nylon filter represents nitric acid released by the volatilization of ammonium nitrate, then an equal molar amount of ammonia should be released. A portion of this may be quickly neutralized on the Teflon filter by acidic deposits. The finding of ammonium on the citric acid coated-filters suggests that a portion of the volatilized ammonia is released along with the nitric acid vapor. For the 4 weeks of available data, 57 ± 26 percent of the ammonia in the volatilized NH_4NO_3 was recovered on the citric acid-coated filter, and 43 percent was apparently retained on the Teflon filter. Additional work is needed to explore more fully the interaction of the NH_4NO_3, NH_3, and HNO_3 in the ADS and TFR.

H^+ and Ion Balances

The hydrogen ion concentrations in the Teflon filter extracts (H^+ Teflon) from the ADS and TFR were examined. On the average, those from the ADS (29.6 ± 15.3 $nmol/m^3$) exceeded those from the TFR (22.5 ± 16.7 $nmol/\ m^3$) by 7.1 $nmol/m^3$. At a pH of 5.0, this difference is equivalent to approximately 0.23 pH units and is significant at the 95 percent confidence level. In contrast, no significant difference was found for the hydrogen ion concentrations in the cyclone extracts from the ADS and TFR.

The ratio of the sum of the measured equivalents of cations (hydrogen ion and ammonium) to the sum of the measured equivalents of anions (sulfate and nitrate) was determined for the cyclone and Teflon filter extracts of the ADS and TFR. The ratio approaches unity for the

Teflon filter extracts. For the TFR, the mean ratio is 1.085 ± 0.086, and for the ADS this value is 0.931 ± 0.142. The two ratios are significantly different at the 95 percent confidence level. This difference may be related to the ammonium artifact found with the TFR or the difference in large particle transmission of the cyclones in the two samplers.

The ion ratios were examined for weekly ADS samples. For 12 weeks of replicate samples the mean ratio is 0.767 ± 0.129. The difference between the weekly and daily ratios is significant and may indicate increased importance of unmeasured cations for 1-week versus 1-day sampling durations.

Ion ratios were examined for cyclone extracts. Although the ratios are appreciably lower for cyclone extracts than for Teflon filter extracts, they are not significantly different across samplers. For daily samples, the mean ratios are 0.272 ± 0.148 with the TFR and 0.286 ± 0.261 with the ADS. For weekly ADS samples, the mean ratio is 0.192 ± 0.086. These findings point toward an increased contribution of unmeasured cations in the cyclone extract over those found on the Teflon filter. This is consistent with the increased contribution of crustal salts found in the large particle size range.

Collection of SO_2 on TFR Nylon Filter

A small portion of SO_2 passing through a nylon filter is retained and may be recovered as sulfate. To address this issue in the current study, sulfate results from the nylon filter extract of the TFR were examined. The equivalent mean concentration is 0.479 ± 0.116 μg SO_4^{2-}/m^3. This amounts to 11.6 ± 8.8 percent of the SO_2 sampled by the TFR. The SO_2 collected on the nylon filter of the TFR is poorly correlated with the total SO_2 collected by the TFR (r = 0.191). The data suggest that nylon retains a relatively constant amount of SO_2 as sulfate. In daily samples, this portion can be substantial (e.g., 12 percent) and should be accounted for when using the TFR to infer daily ambient SO_2 concentrations. This correction has been made to the TFR SO_2 results reported in the current study.

Nitrite on TFR Nylon Filter

A small amount of nitrite was found on the nylon filter in the TFR. The amount corresponds to 0.056 ± 0.038 $\mu g/m^3$. Since laboratory experiments have indicated that nylon can collect HONO and retain it as nitrite (see Appendix A), the nitrite on the TFR nylon filters was compared to the ADS HONO concentrations. These two data sets are poorly correlated (r = -0.274). As a result, it appears that in the TFR, HONO is removed from the sample upstream of the nylon filter, is not collected by the nylon filter, or is not recoverable from the nylon filter.

Conversion of Nitrite to Nitrate in ADS

The ratio of the weekly average concentration computed from the sum of the short duration daily samples to the long duration weekly samples can be used to indicate when sampled species are stable or react following collection. Sulfur dioxide is relatively stable and shows a ratio of 0.96. Nitrous acid with a ratio of 16.5 is apparently unstable, while Total NO_3^- with a ratio of 0.79 and HNO_3 with 0.88 may also be unstable. A ratio exceeding unity (e.g., HONO) may indicate that the collected species is converted to another species more completely during the long duration sampling period than during the short duration sampling periods. A ratio less than unity (e.g., Total NO_3^- and HNO_3) may indicate that another cocollected species is converted to the species under consideration preferentially during the long duration sampling. A possible explanation for the high ratio for HONO and the low ratios for Total NO_3^- and HNO_3 is that the NO_2^- collected from HONO and other NO_x species is converted during the week-long sampling period to NO_3^-. The increase in NO_3^- between the summed daily and weekly HNO_3 accounts for 28 percent of the NO_2^- decrease (as NO_3^-) between the summed daily and weekly HONO samples. When the amount of lost NO_2^- between the summed daily and the weekly HONO samples is converted to NO_3^- and added to the summed daily Total NO_3^-, the resulting ratio is 0.97. This provides evidence supporting the hypothesis of conversion of NO_2^- to NO_3^- in the weekly ADS samples.

The mass found on the second denuder and the percent contribution of the mass on the second to the sum on the first and second denuders is given in Table 17 for nitrite, nitrate, and sulfate for both daily and weekly samples. Since approximately 2 percent of the sulfate on the two denuders is found on the second denuder, the first denuder is at least 98 percent efficient for collecting SO_2. This efficiency could be higher, if part of the sulfate on the second denuder is contributed by deposited particulate sulfates. Comparable collection efficiencies are also to be expected for HONO and HNO_3, but the contributions of the mass of both NO_2^- and NO_3^- on the second denuders exceed 2 percent of the respective totals. This suggests that other gas and/or particulate NO_2^- and NO_3^- species are deposited on the second denuder.

On the average, the mass of a species on the second denuder from the weekly samples should be seven times greater than the average value for the daily samples. This ratio is 9.3 for SO_4^{2-}, 1.5 for NO_2^-, and 24 for NO_3^-. If it is assumed that the weekly NO_2^- should be 9.3 times higher than the daily value, then 16.8 μg NO_2^- (22.6 μg as NO_3^-) is lost in the weekly sample. Assuming that the weekly NO_3^- should be 9.3 times higher than the daily value, then an excess of 28.2 μg NO_3^- is present in the weekly sample. The mass of lost NO_2^- agrees very well with the excess of NO_3^- on the second denuder.

These findings indicate that for the ADS, sulfates are stable, the sum of nitrates and nitrites is stable, and that collected nitrites are converted to nitrates in the weekly samples. This conversion of nitrites to nitrates suggests that weekly ADS samples may overestimate ambient HNO_3 concentrations and underestimate ambient HONO concentrations.

TABLE 17. MASS AND PERCENT CONTRIBUTION OF SPECIES RECOVERED FROM SECOND DENUDER

	Daily		Weekly[a]		Mass Ratio
Species	Mass[b]	Contribution[c]	Mass	Contribution	Weekly/Daily
NO_2^-	2.17 ± 1.55	9.8 ± 3.6	3.29 ± 2.30	16.2 ± 15.3	1.5
NO_3^-	1.92 ± 1.08	5.7 ± 2.2	46.10 ± 36.16	14.6 ± 1.8	24.0
SO_4^{2-}	2.79 ± 2.16	2.0 ± 1.8	25.98 ± 7.34	2.2 ± 0.1	9.3

[a] For the two weeks encompassing the daily samples.

[b] Average mass of indicated species on second denuder expressed as µg.

[c] Calculated as 100 times the mass of indicated species on second denuder divided by sum of masses on first and second denuders expressed as percent.

Comparison of ADS and TFR Results

Concentration and Precision Results--

Concentration and precision results for the ADS and TFR samplers are summarized in Table 18. The tabulated parameters include: total gaseous and particulate ammonia and ammonium (Total NH_3+NH_4^+), fine particle ammonium (Fine NH_4^+), and ammonia (NH_3); hydrogen ion collected on the Teflon filter (H^+ Teflon); total gaseous and particulate nitric acid and nitrate (Total NO_3^-); fine particle nitrate (Fine NO_3^-), nitrate collected on the Teflon filter (NO_3^- Teflon), nitric acid (HNO_3), nitrous acid (HONO), and nitrogen dioxide (NO_2); and total particulate sulfate (Total SO_4^{2-}), fine particle sulfate (Fine SO_4^{2-}), and sulfur dioxide (SO_2). The term "total" indicates that the cyclone catch for that species is included. The term "fine" refers to particles passing the cyclone and entering the Teflon filter in the particulate phase. Studywide estimates of mean and standard deviations of each parameter are given for each sampler. Within day and within week median differences and coefficients of variation are also given, where available, for the two samplers. These differences and CV's provide insight on the sampling and analysis precision typically associated with each of the samplers.

The TFR Fine NO_3^- results are negative in 24 of 26 cases. As a result, they do not permit meaningful comparisons and are not considered in subsequent data analyses.

In general, both the ADS and TFR show good precision for all parameters. In all cases, the median difference between the paired ADS daily samples is less than 0.2 $\mu g/m^3$, and with two exceptions, the corresponding results for the TFR are less than 0.5 $\mu g/m^3$. With only two exceptions, TFR HNO_3 and TFR H^+ Teflon, the median CV's are less than 20 percent. The median CV's for the Total NH_3+NH_4^+, Total NO_3^-, and Total SO_4^{2-} are all less than 5 percent. This shows excellent within sampler precision for both the ADS and TFR.

Since colorimetric ammonium analysis was more variable than the IC analyses, the relatively high median CV's for NH_3 in each sampler may be reflecting the large analytical variability for NH_4^+ at the low concentrations associated with ambient NH_3. This is also apparent in the weekly results. In addition, weekly mean NH_3 concentrations appear substantially lower than the mean daily values. This may reflect differences caused by seasonal variation in the ambient NH_3 concentration.

The pH analysis of Teflon filter extracts resulted in appreciable variability of the H^+ Teflon in both samplers. This is not surprising when it is noted that a difference in pH of 0.25 at a pH of 5.00 can propagate a difference of 7.8 n mol H^+/m^3.

Substantial differences in the partitioning of nitrate occur on the Teflon and nylon filters. This is reflected consistently for the ADS in both daily and weekly samples.

The TFR uses a nylon strip to collect a fixed fraction (8.5 percent) of the sampled nitric acid. Substantially more variability is apparent in the TFR estimates of HNO_3 than is apparent in the ADS results.

The weekly ADS HONO concentrations showed more variability than is evident in the daily samples. In addition, the weekly mean HONO concentration appears lower than the mean daily values. This may reflect differences caused by seasonal variation in the ambient HONO concentration or sample instability as noted elsewhere.

The TFR, sampling only 10 percent of the total flow for SO_2 and NO_2, showed appreciably greater variability in the SO_2 concentration than did the ADS (i.e., 12.8 versus 1.8 percent). It is surprising that similar behavior is not apparent in the TFR NO_2 results, which show a median CV of 3.2 percent.

The results depicted in Figures 11 to 23 show the behavior of the daily means of each of the test parameters for the ADS and TFR over the 13-day intensive study. Similar results illustrating the behavior of weekly means of each test parameter for the ADS are given in Figures 24 to 35.

Sample Stability, A Comparison of Daily and Weekly Results--

Weekly average concentrations were computed using results from the appropriate daily ADS samples. These results were then ratioed to the results of the appropriate weekly samples. The average ratios of computed to measured weekly results for the 2-week period from 9/30/86 to 10/12/86 are also displayed in Table 18. Ratios near unity suggest sample stability across sampling durations of 22 hours to 7 days. Thus, sample stability is indicated for Total NH_3+NH_4^+, Fine NH_4^+, NH_3, Total SO_4^{2-}, Fine SO_4^{2-}, and SO_2 determined, using the ADS, which have average ratios between 0.95 and 1.03.

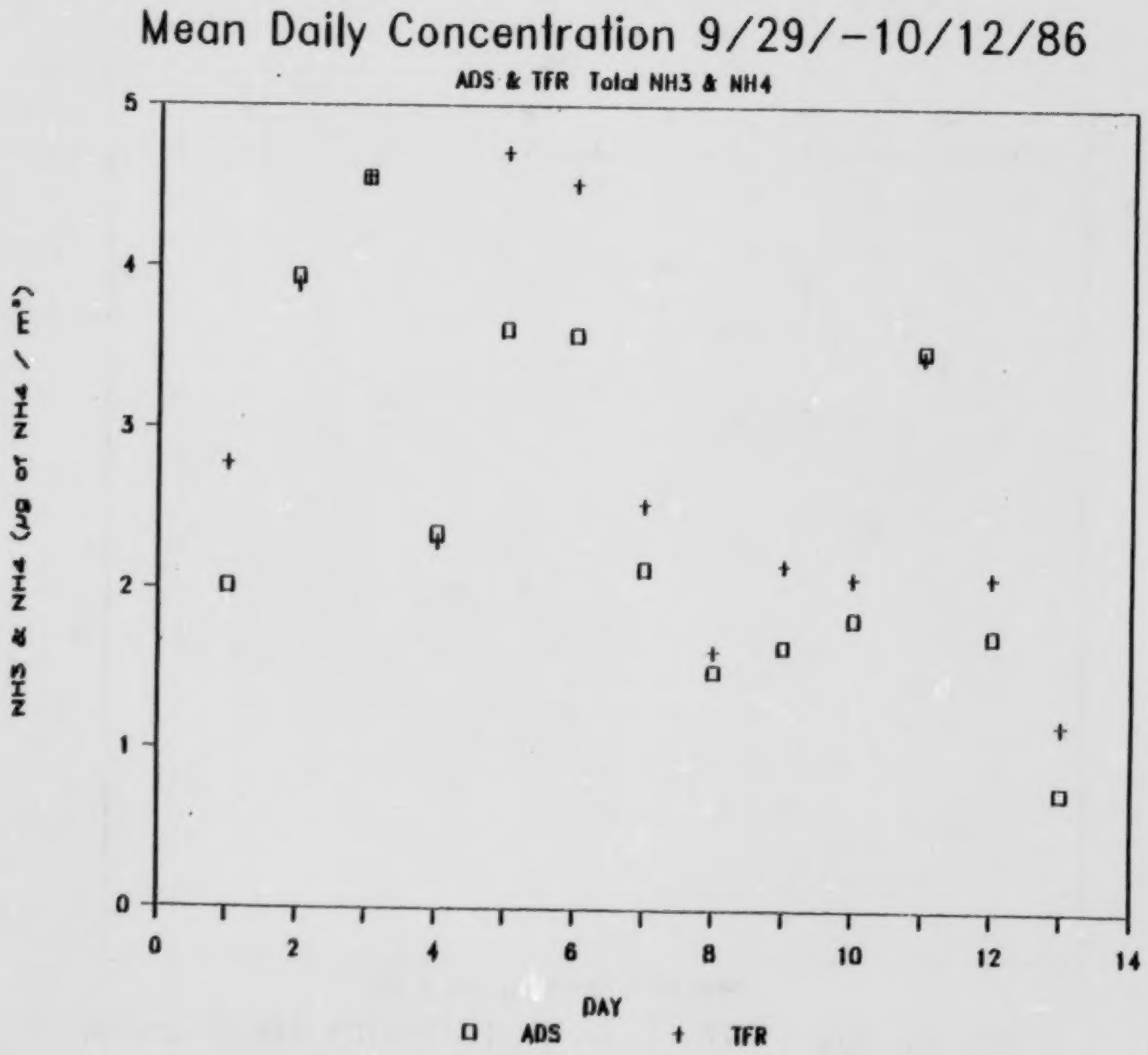


Figure 11. Mean daily Total $NH_3+NH_4^+$ concentrations from ADS and TFR samplers.

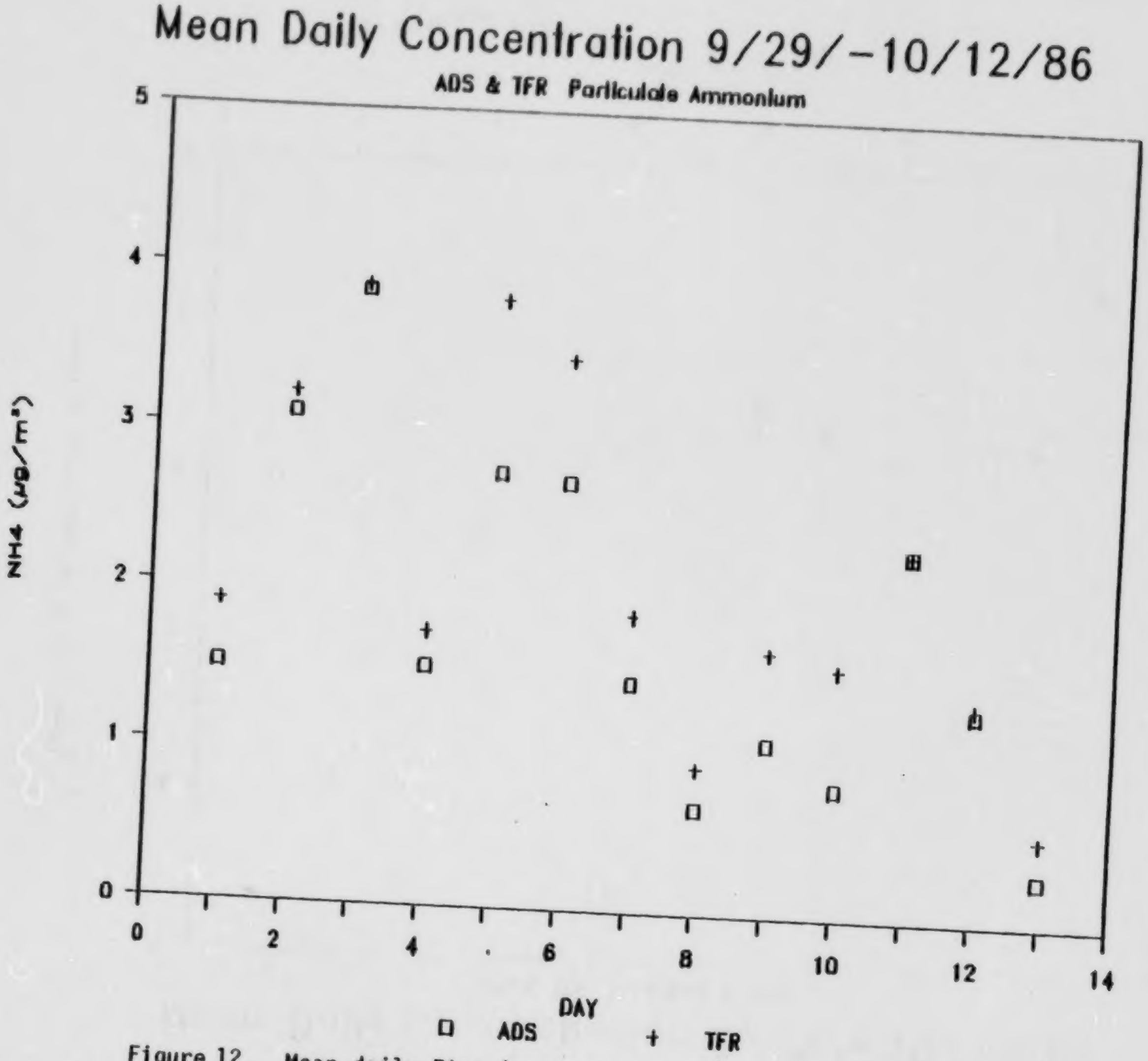


Figure 12. Mean daily Fine (particulate) NH_4^+ concentrations from ADS and TFR samplers.

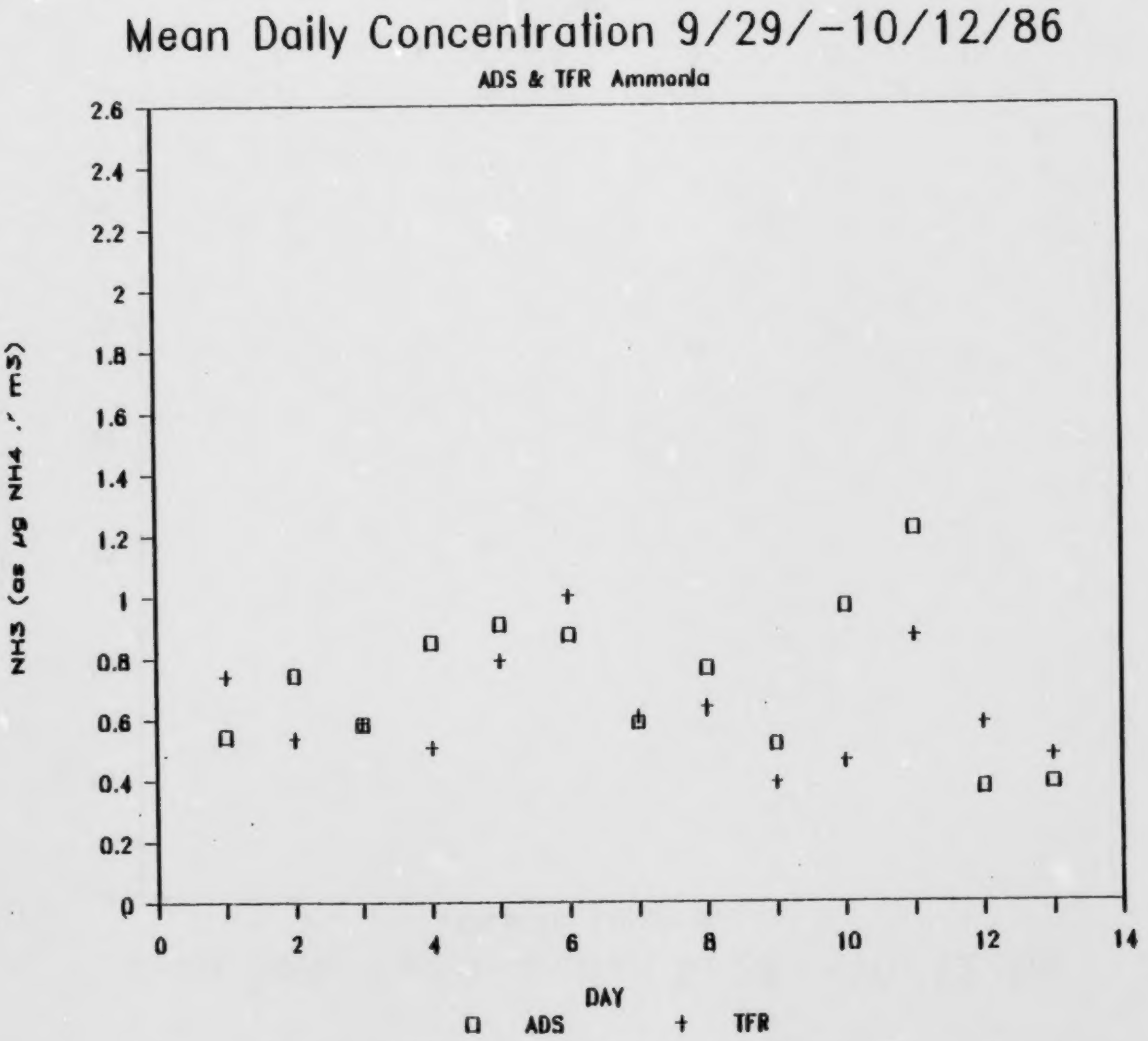


Figure 13. Mean daily NH_3 concentrations from ADS and TFR samplers.

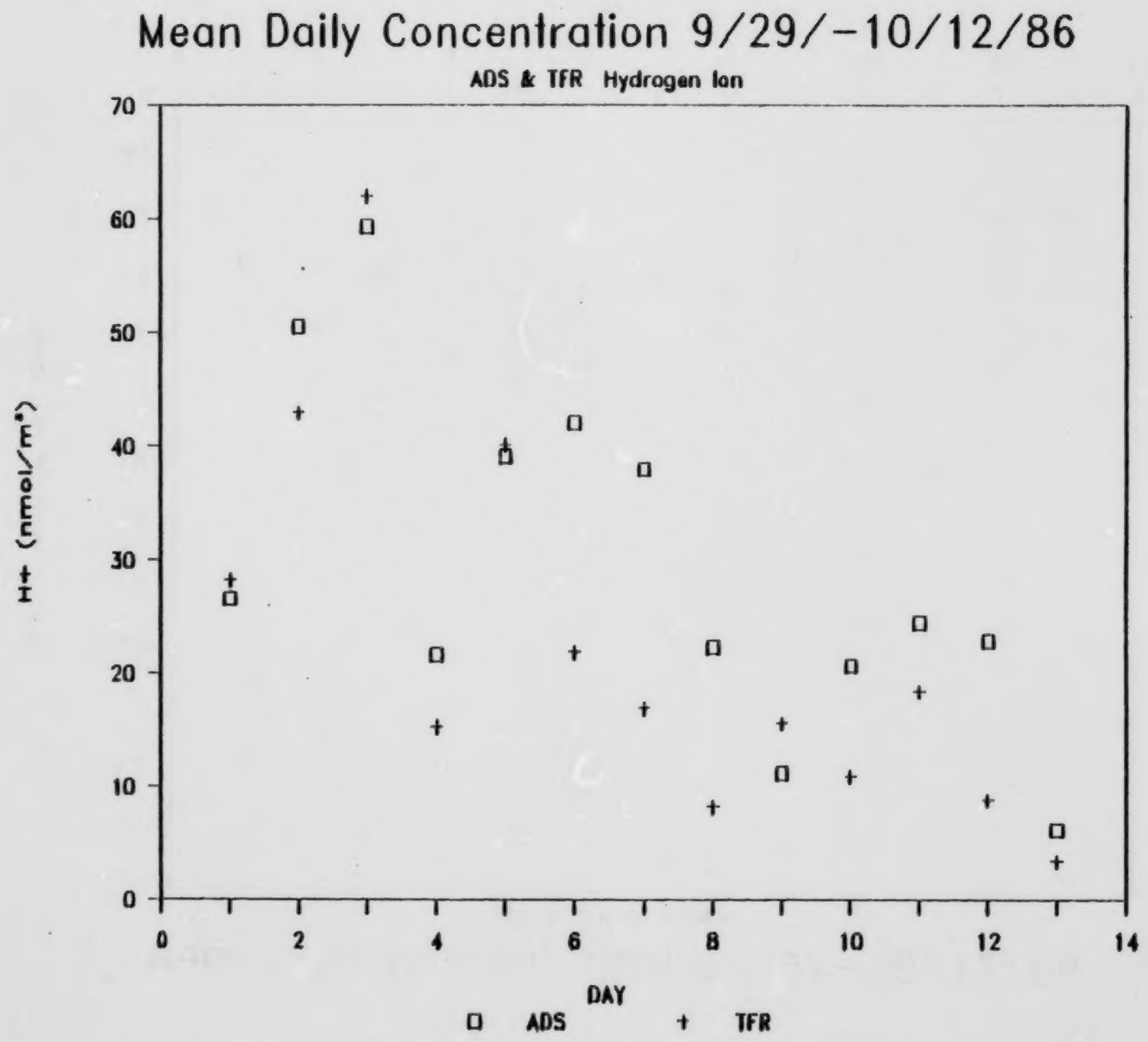


Figure 14. Mean daily hydrogen ion concentrations from the extracts of ADS and TFR Teflon filters.

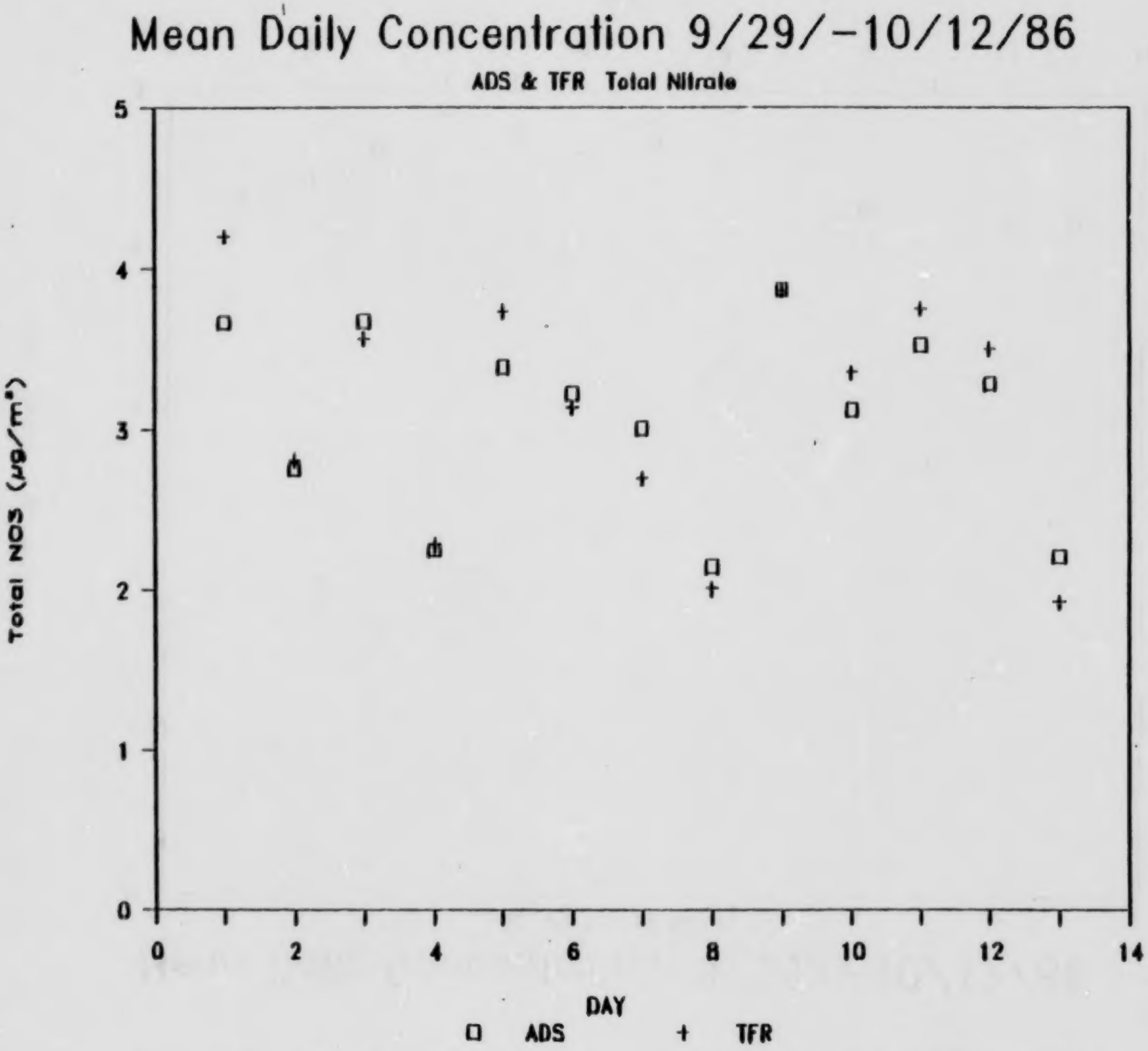


Figure 15. Mean daily Total NO_3^- concentrations from ADS and TFR samplers.

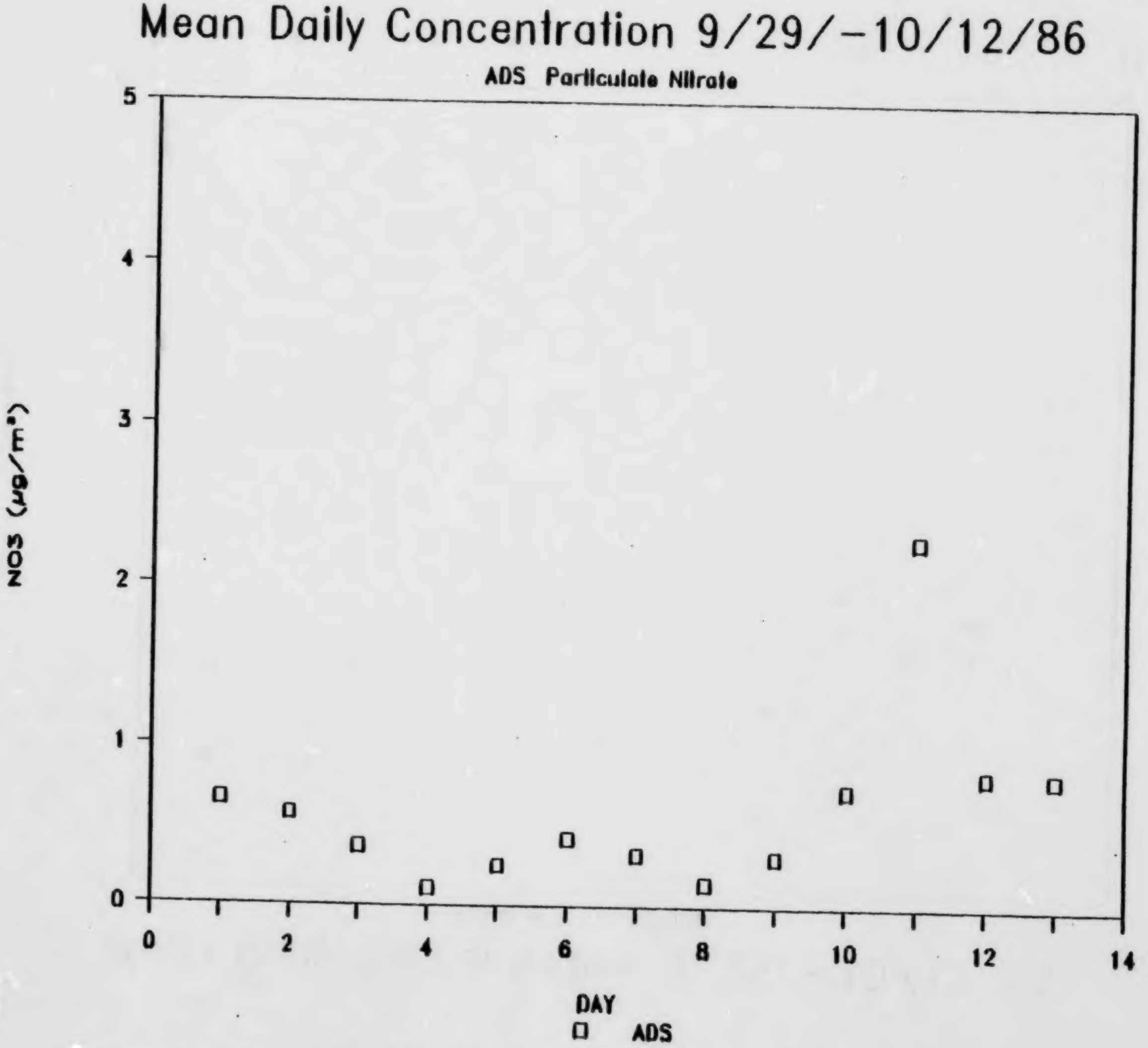


Figure 16. Mean daily Fine (particulate) NO_3^- concentrations from ADS sampler.

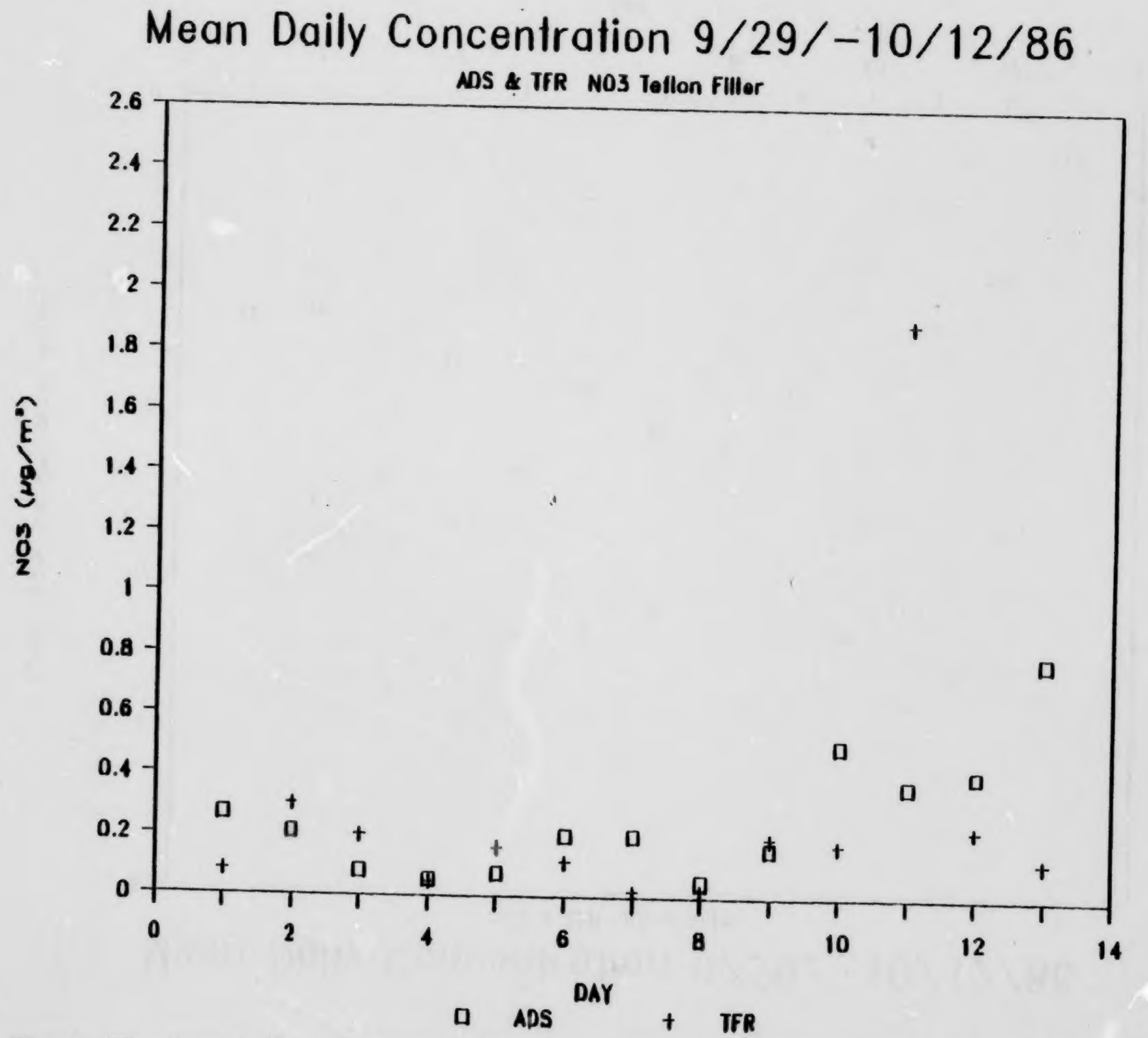


Figure 17. Mean daily NO_3^- concentrations from the extracts of ADS and TFR Teflon filters.

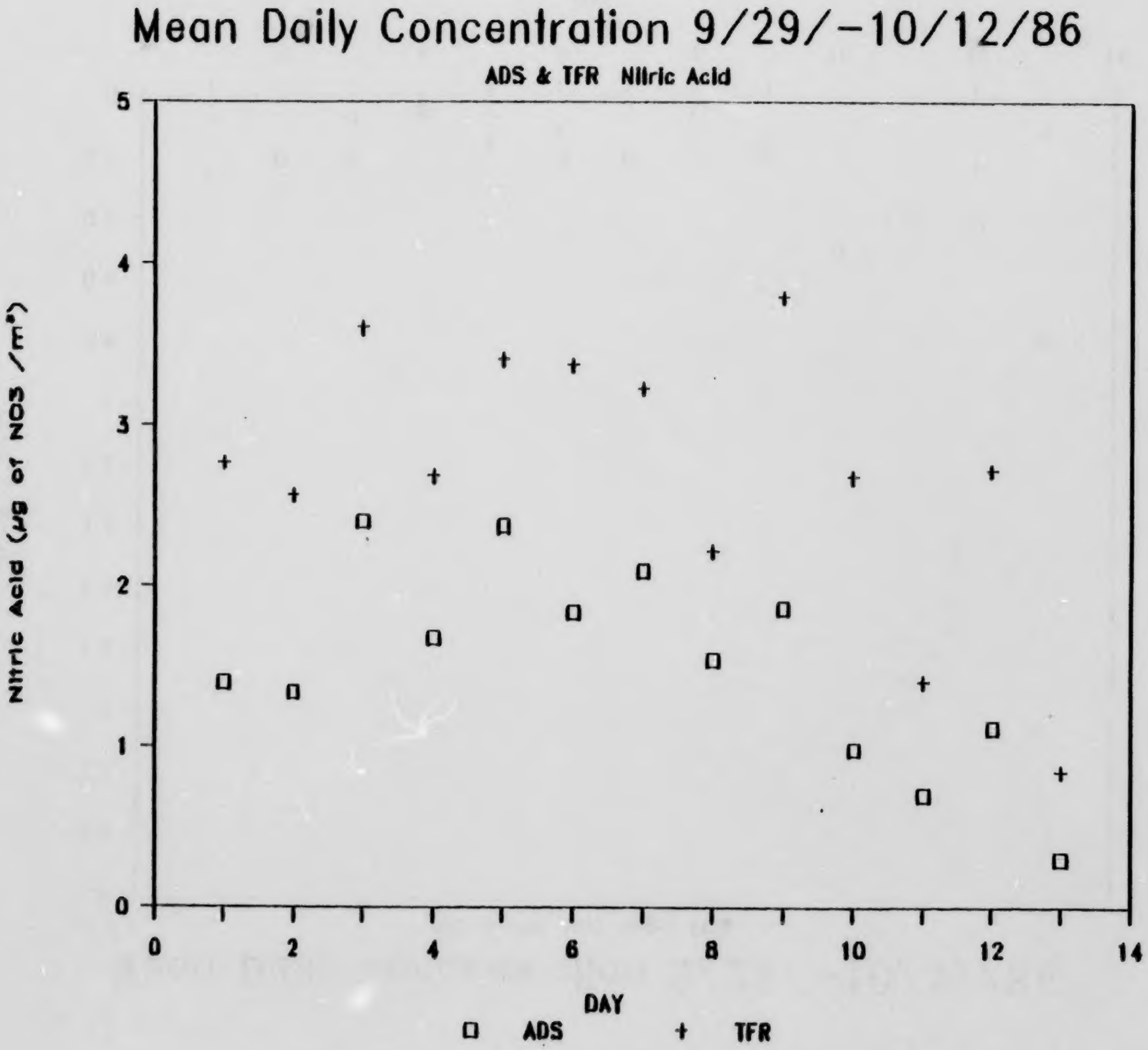


Figure 18. Mean daily HNO_3 concentrations from ADS and TFR samplers.

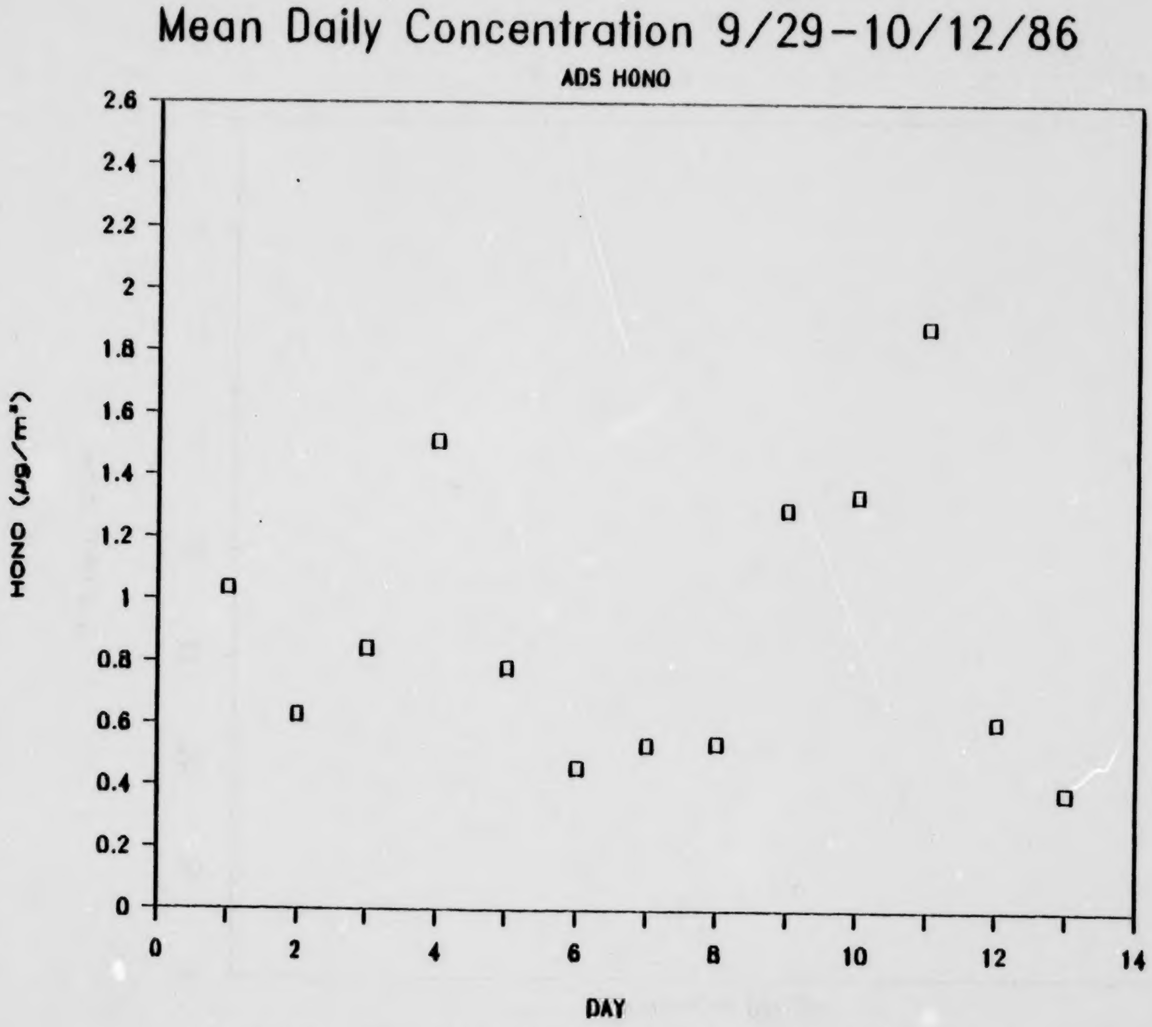


Figure 19. Mean daily HONO concentrations from ADS sampler.

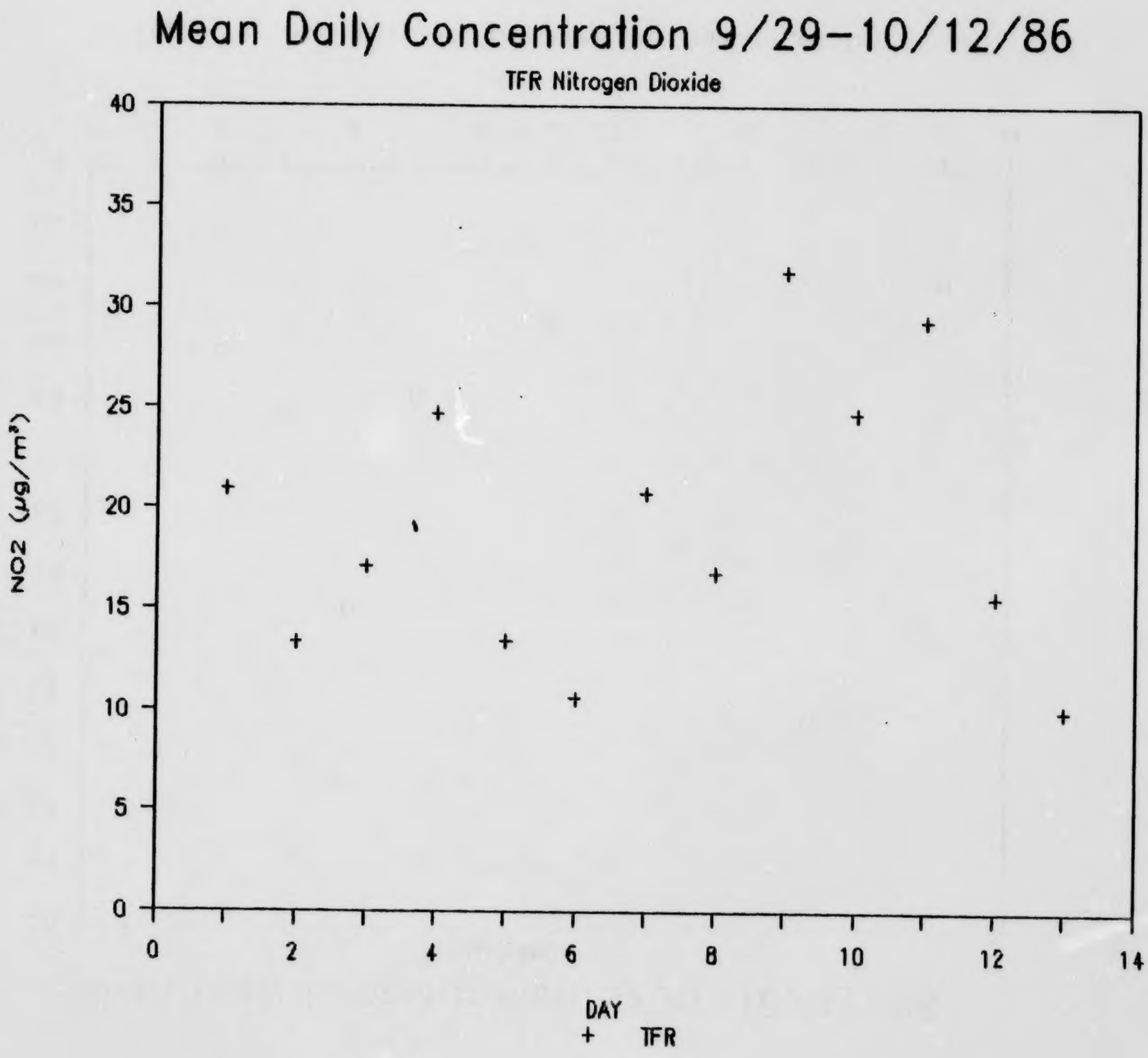


Figure 20. Mean daily NO_2 concentrations from TFR sampler.

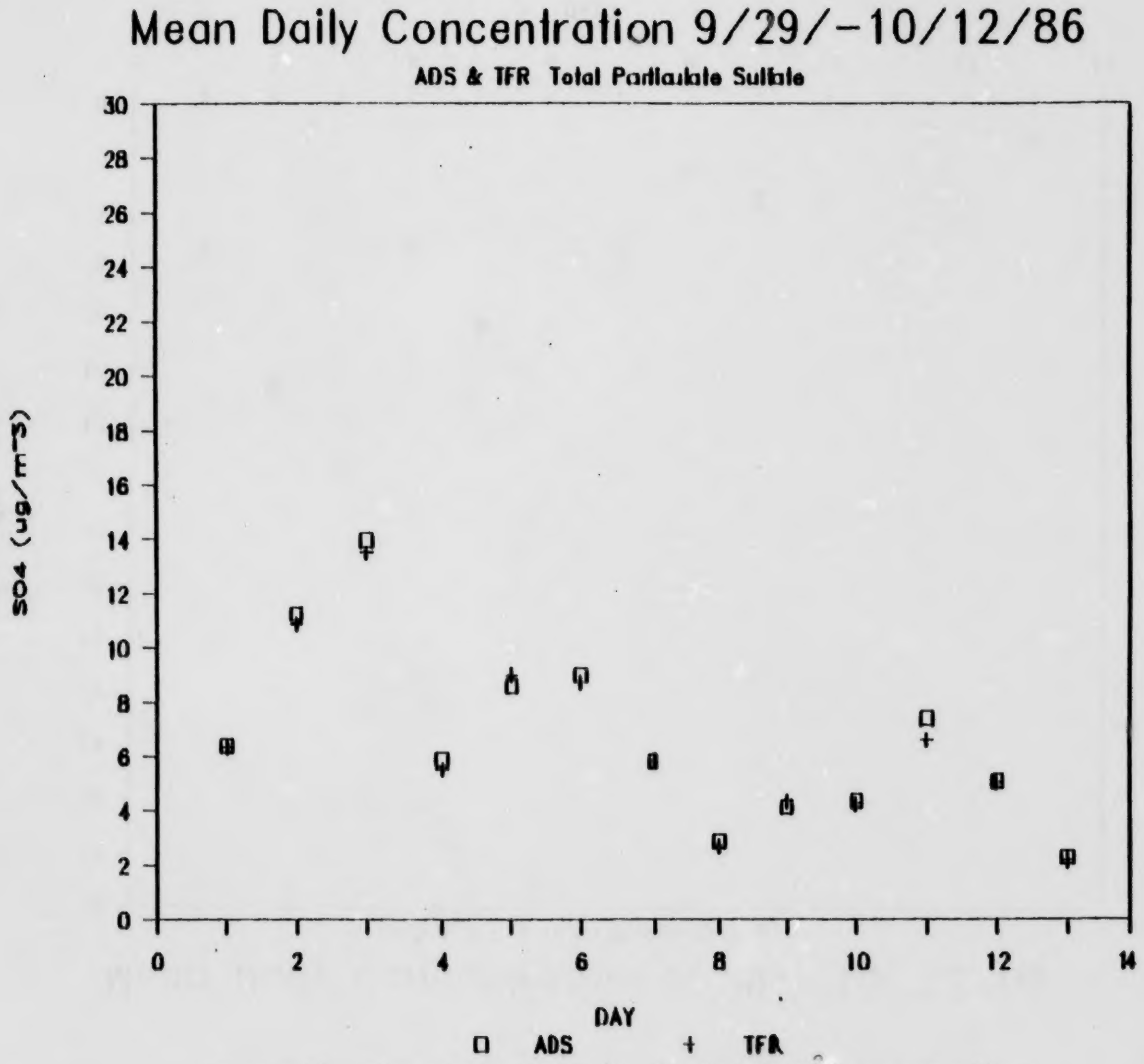


Figure 21. Mean daily Total (particulate) SO_4^{2-} concentrations from ADS and TFR samplers.

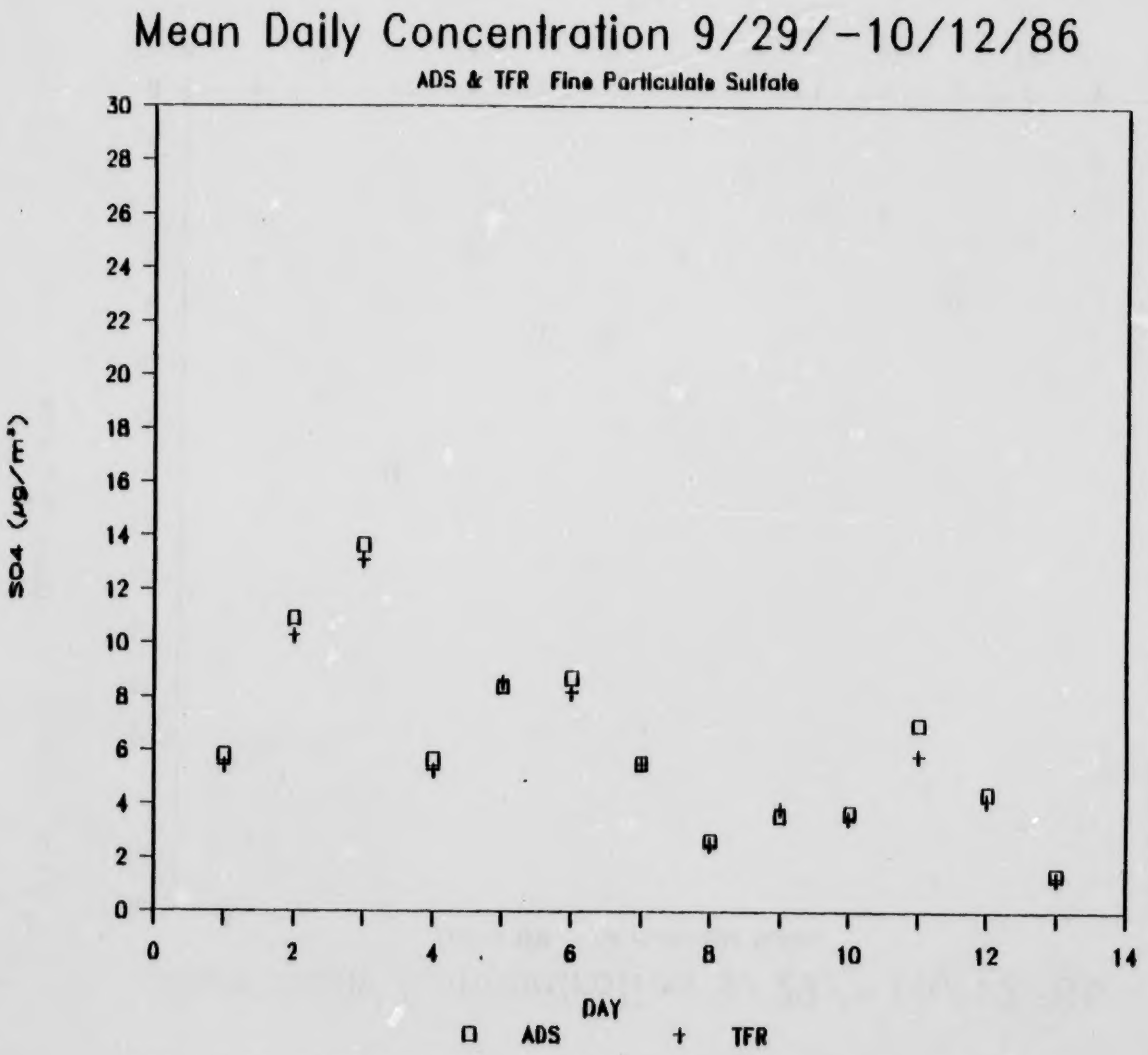


Figure 22. Mean daily Fine (particulate) SO_4^{2-} concentrations from ADS and TFR samplers.

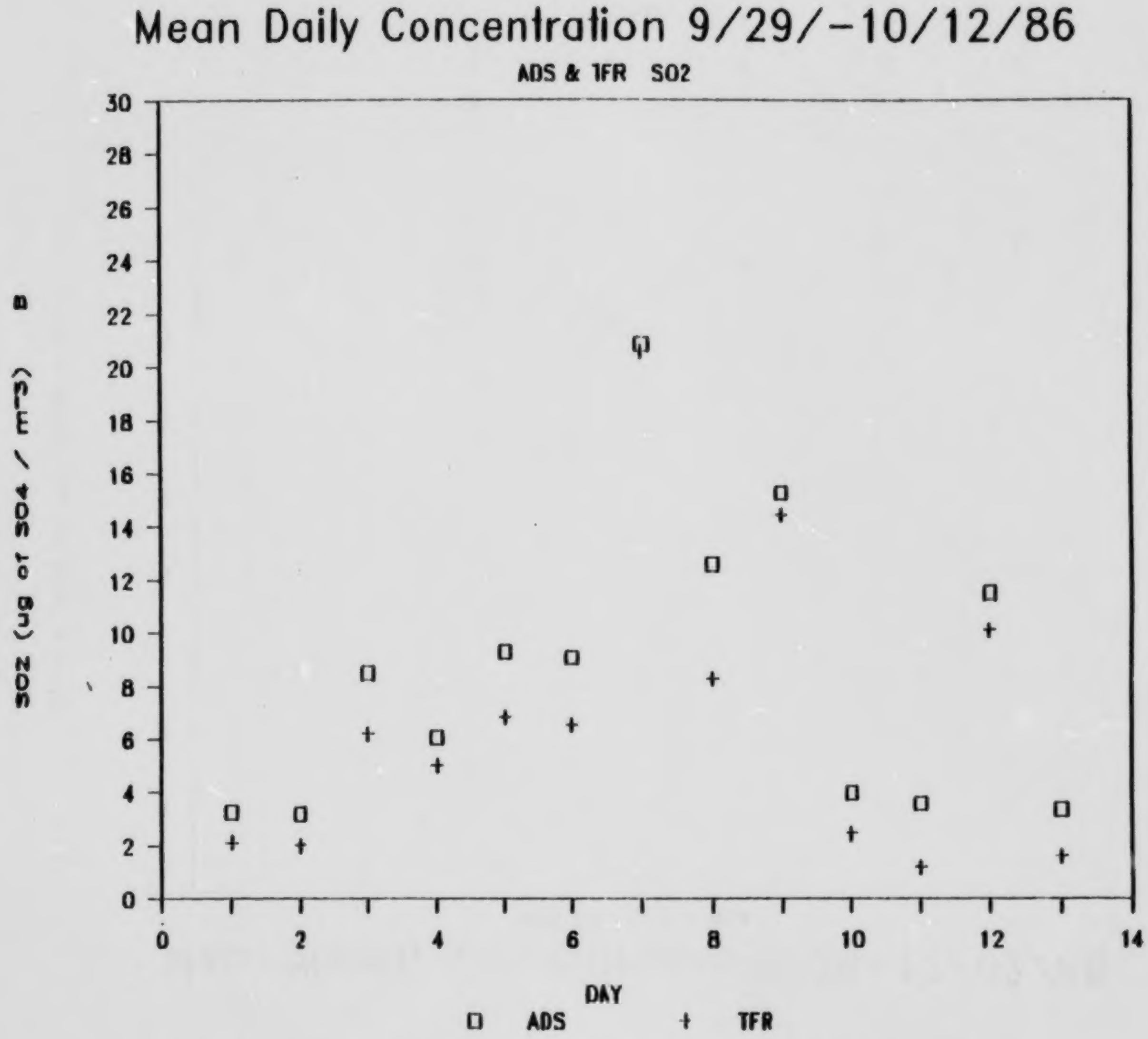


Figure 23. Mean daily SO_2 concentrations from ADS and TFR samplers.

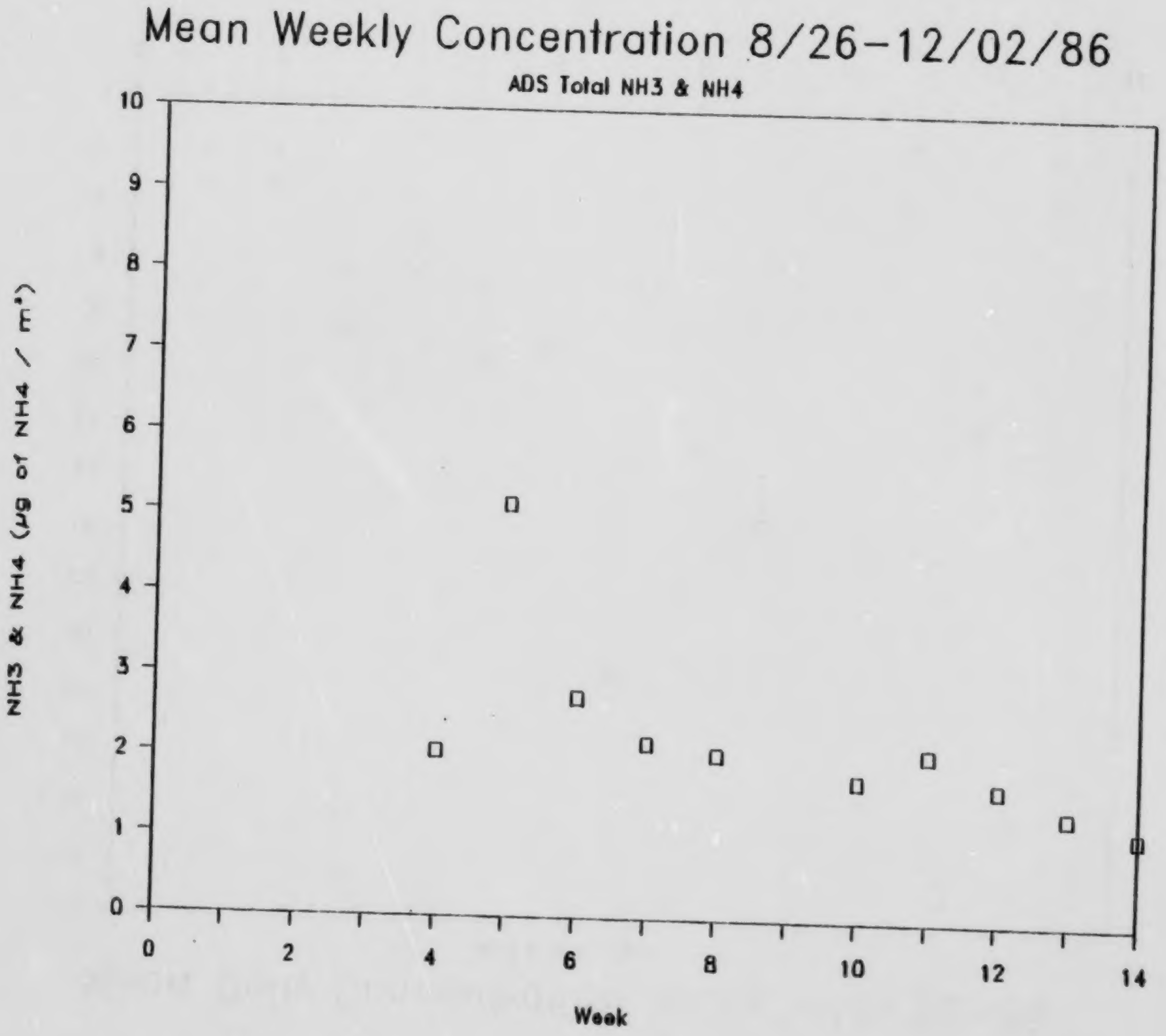


Figure 24. Mean weekly Total $NH_3+NH_4^+$ concentrations from ADS sampler.

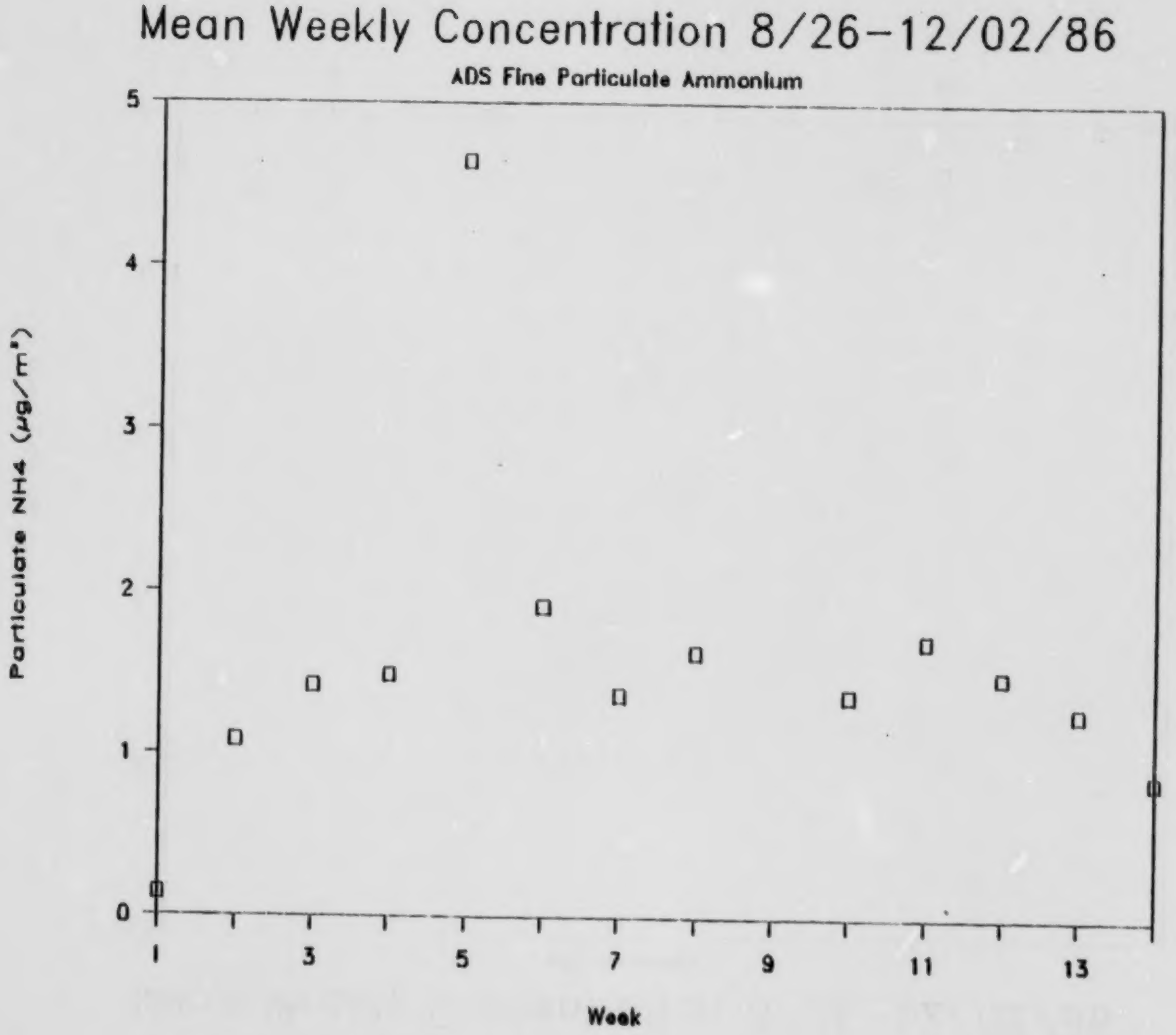


Figure 25. Mean weekly Fine (particulate) NH_4^+ concentrations from ADS sampler.

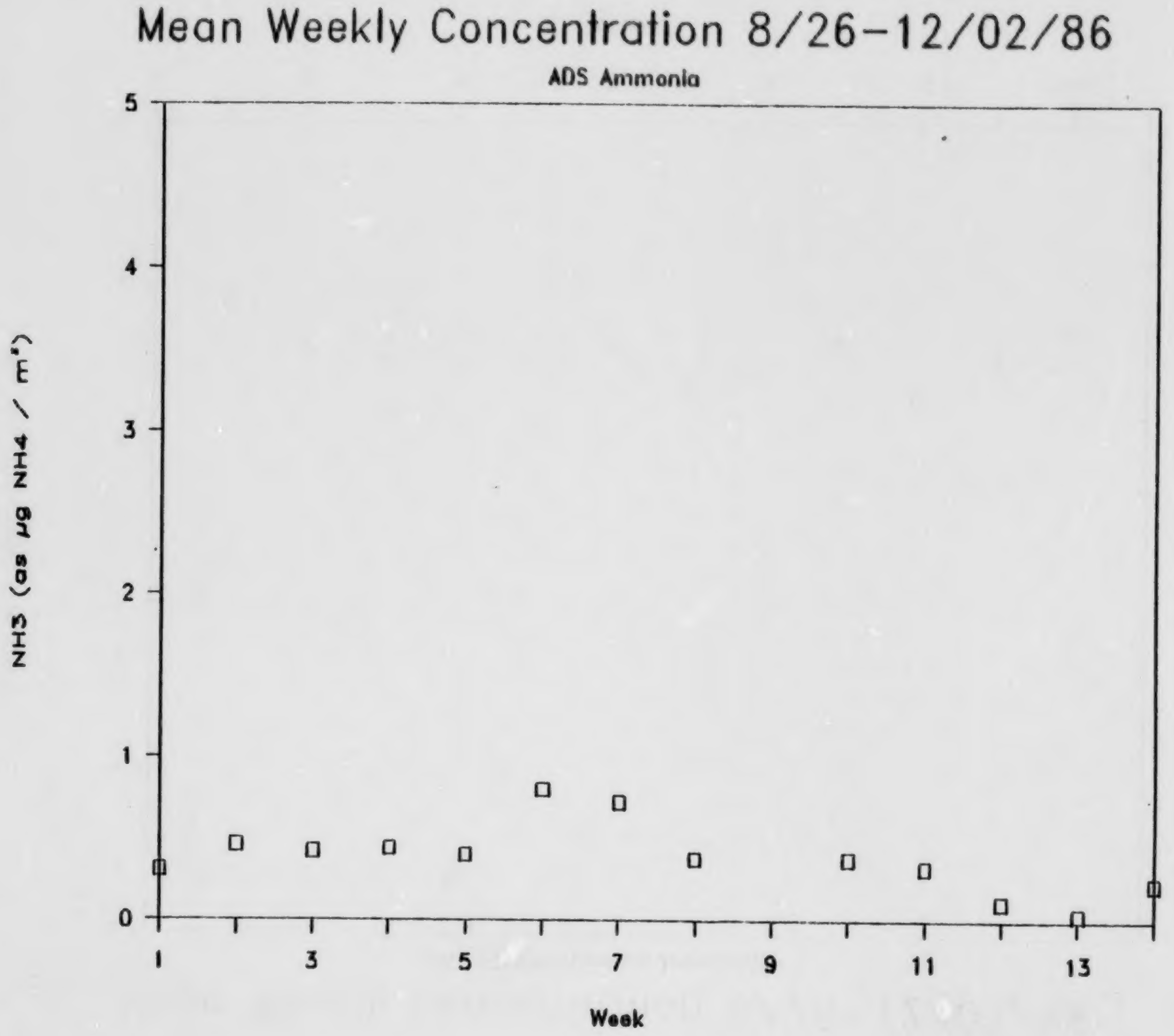


Figure 26. Mean weekly NH_3 concentrations from ADS sampler.

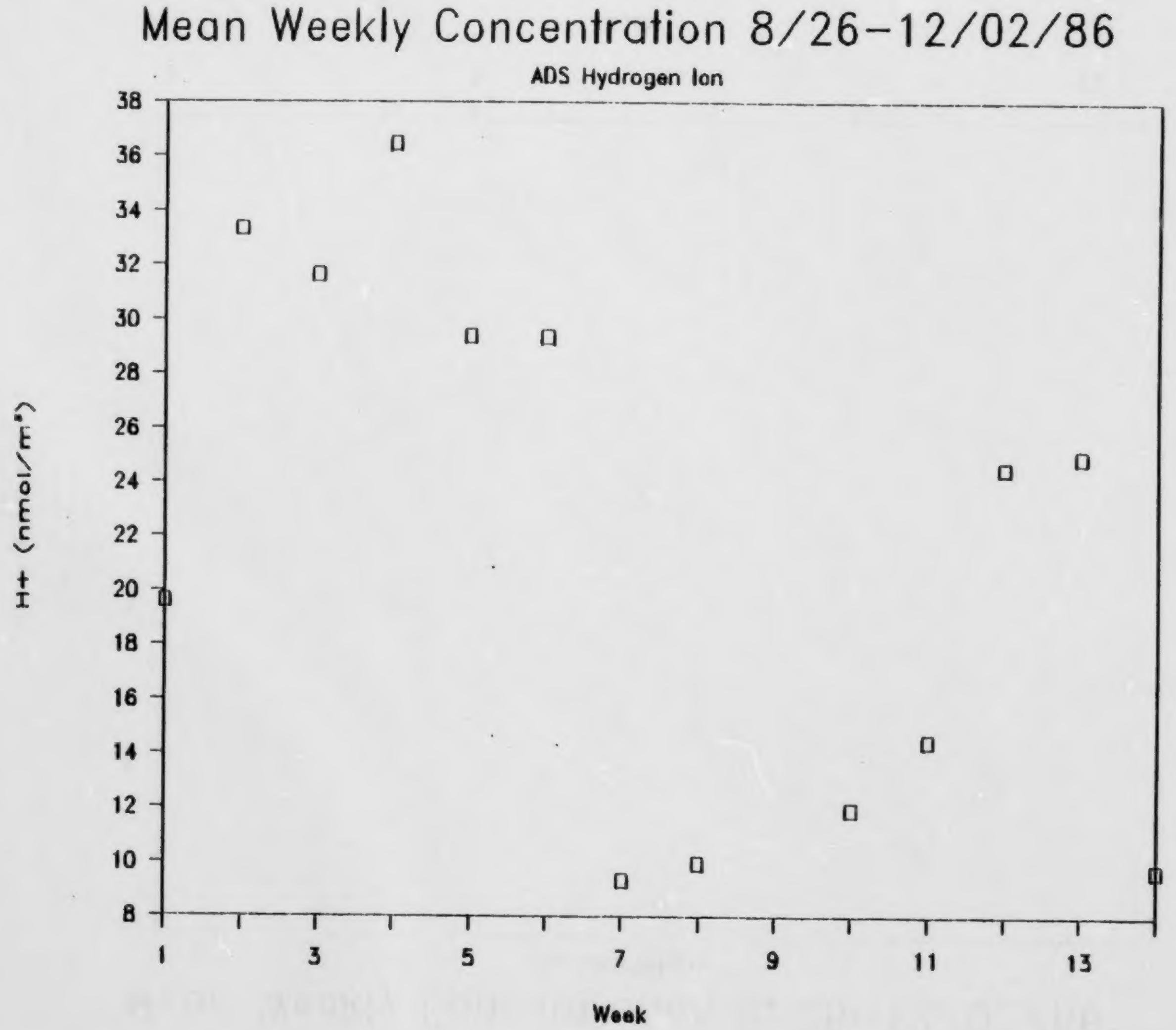


Figure 27. Mean weekly hydrogen ion concentrations from the extracts of ADS Teflon filters.

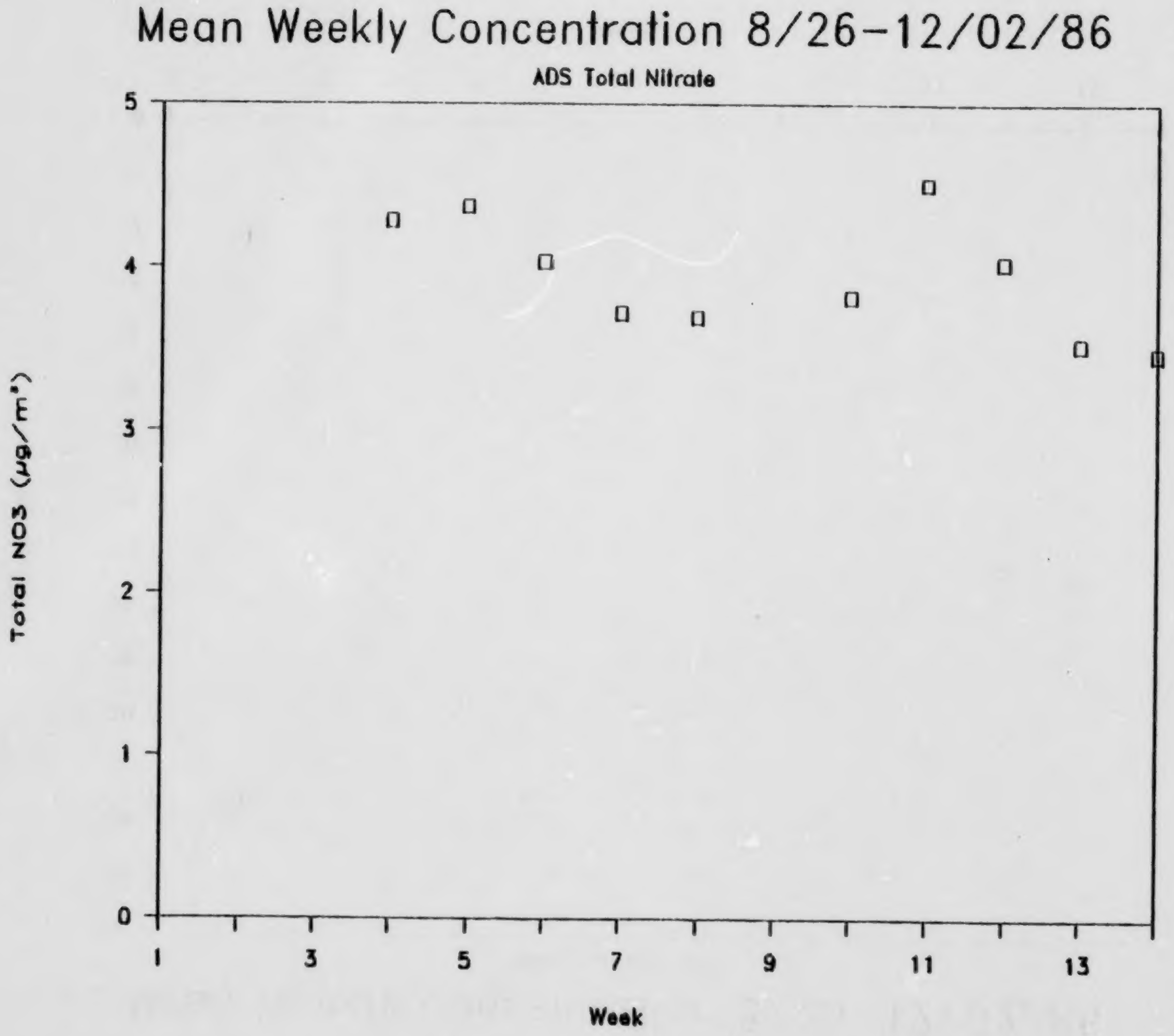


Figure 28. Mean weekly Total NO_3^- concentrations from ADS sampler.

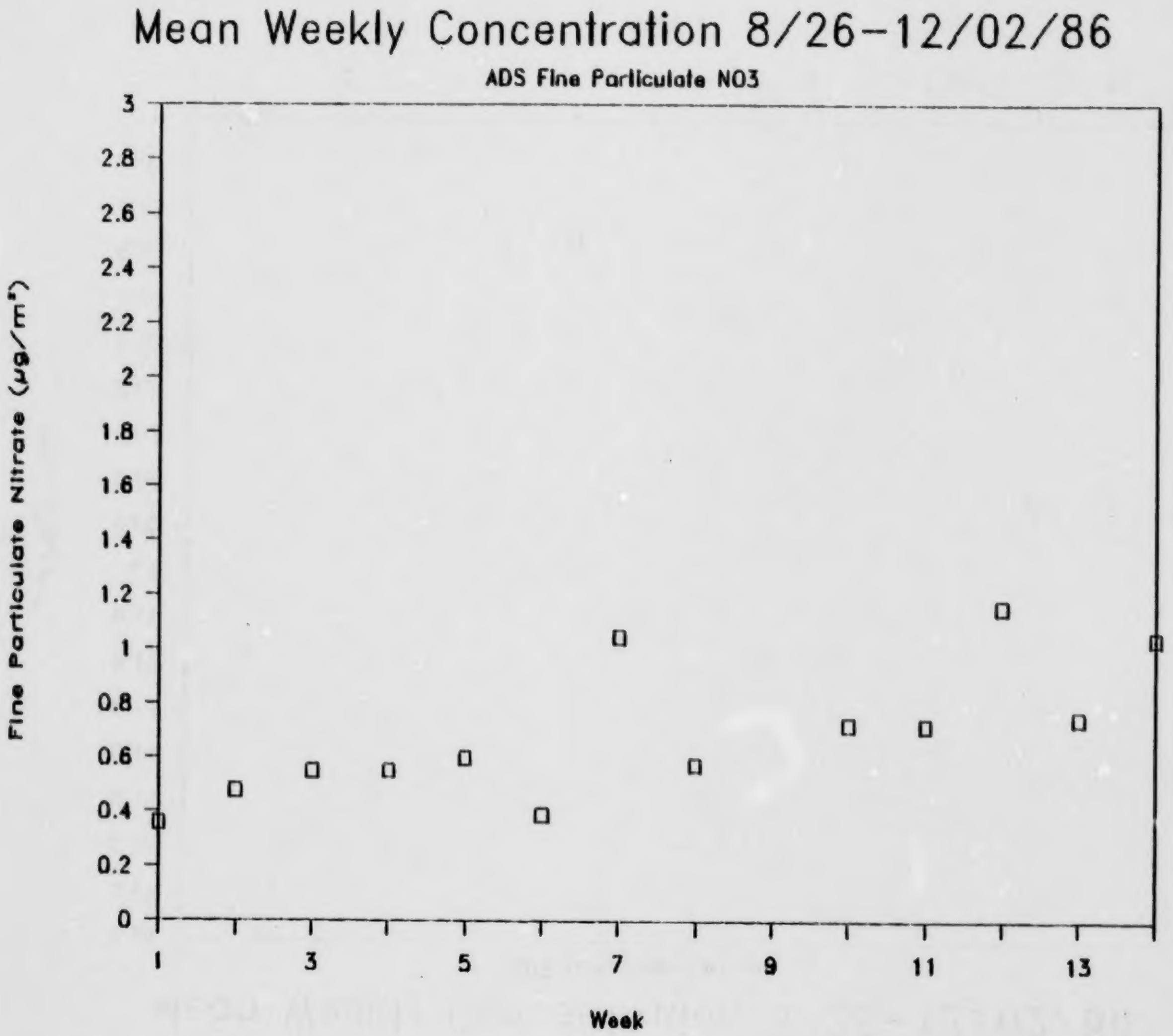


Figure 29. Mean weekly Fine (particulate) NO_3^- concentrations from ADS sampler.

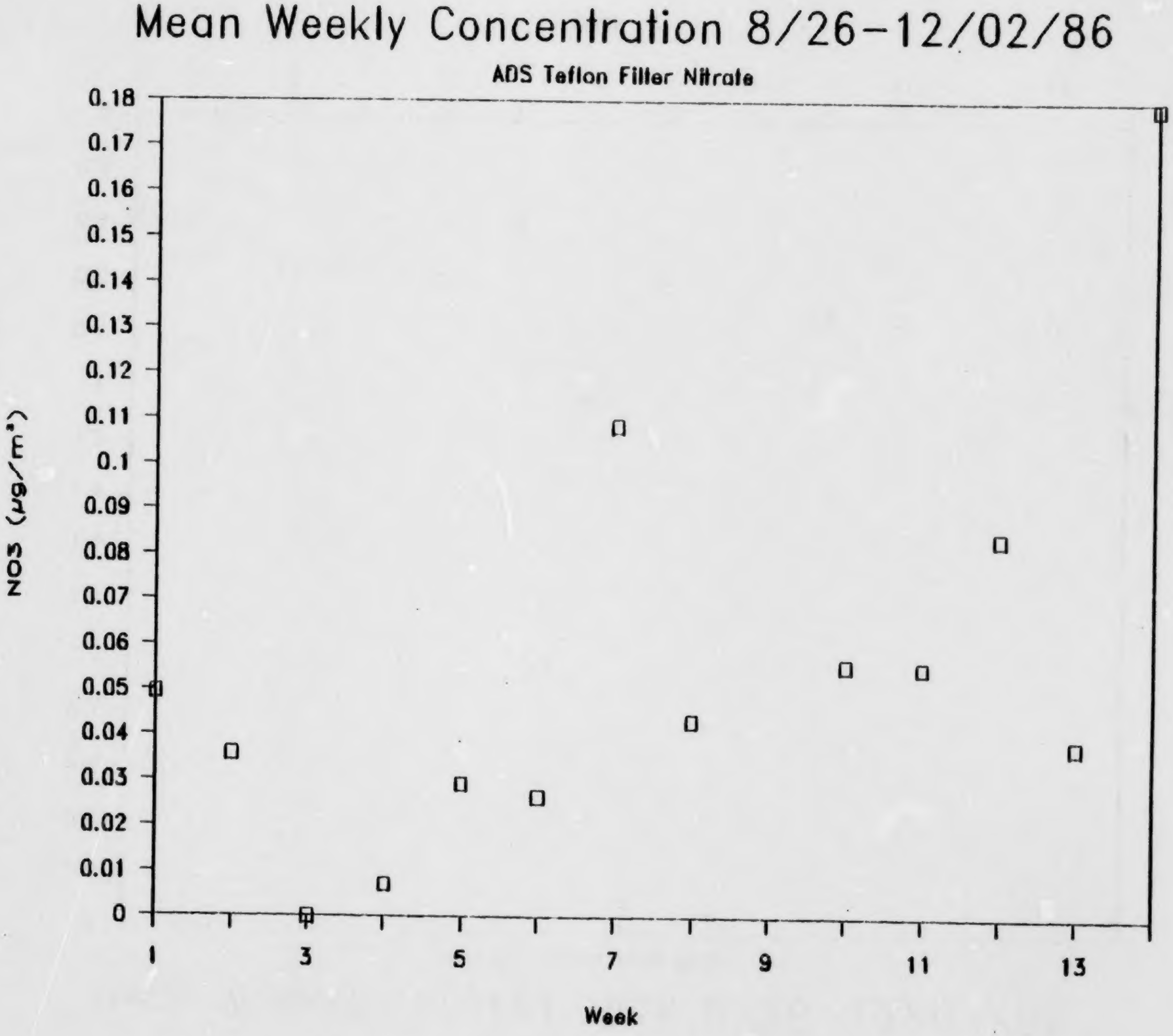


Figure 30. Mean weekly NO_3^- concentrations from the extracts of ADS Teflon filters.

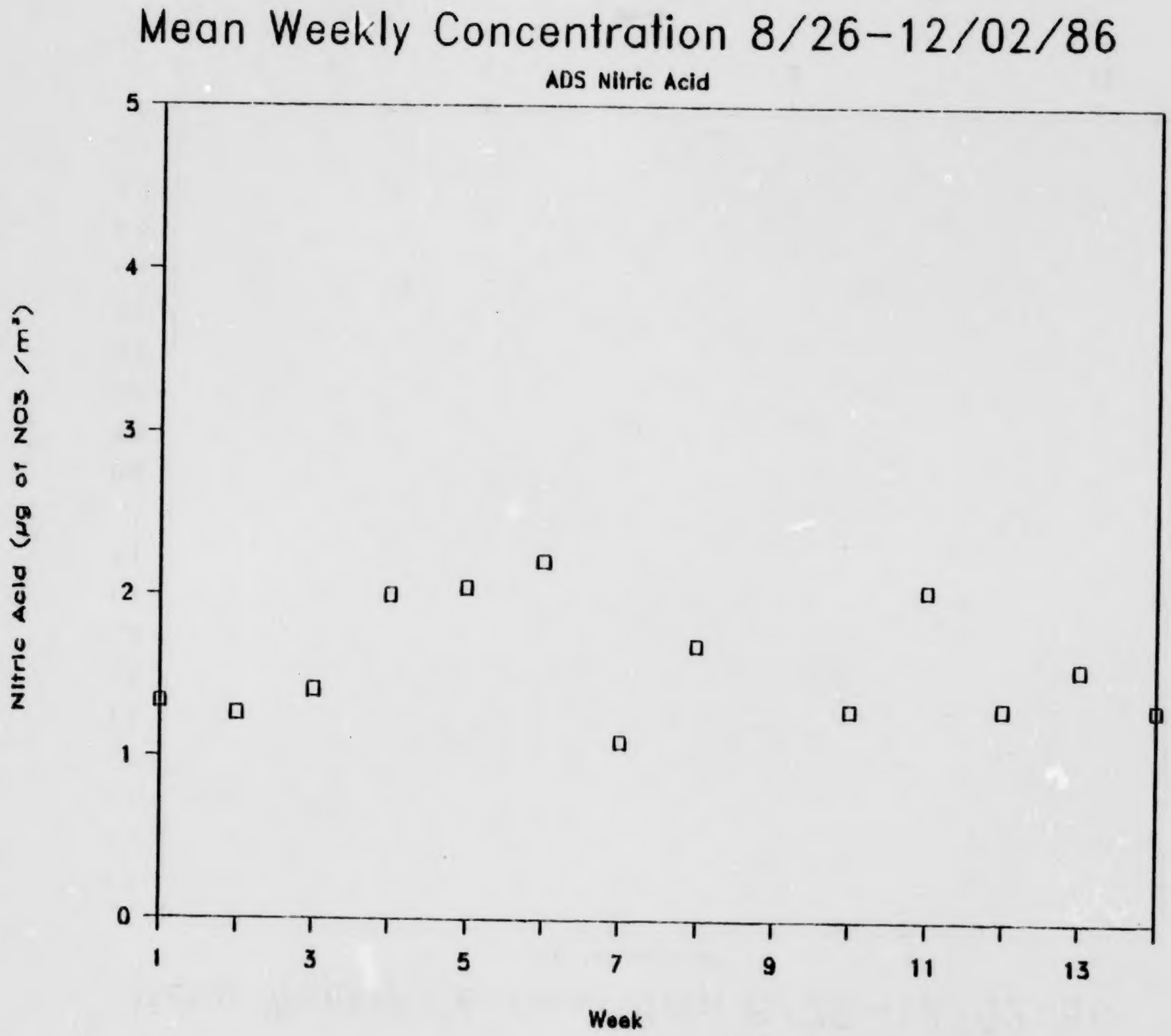


Figure 31. Mean weekly HNO_3 concentrations from ADS sampler.

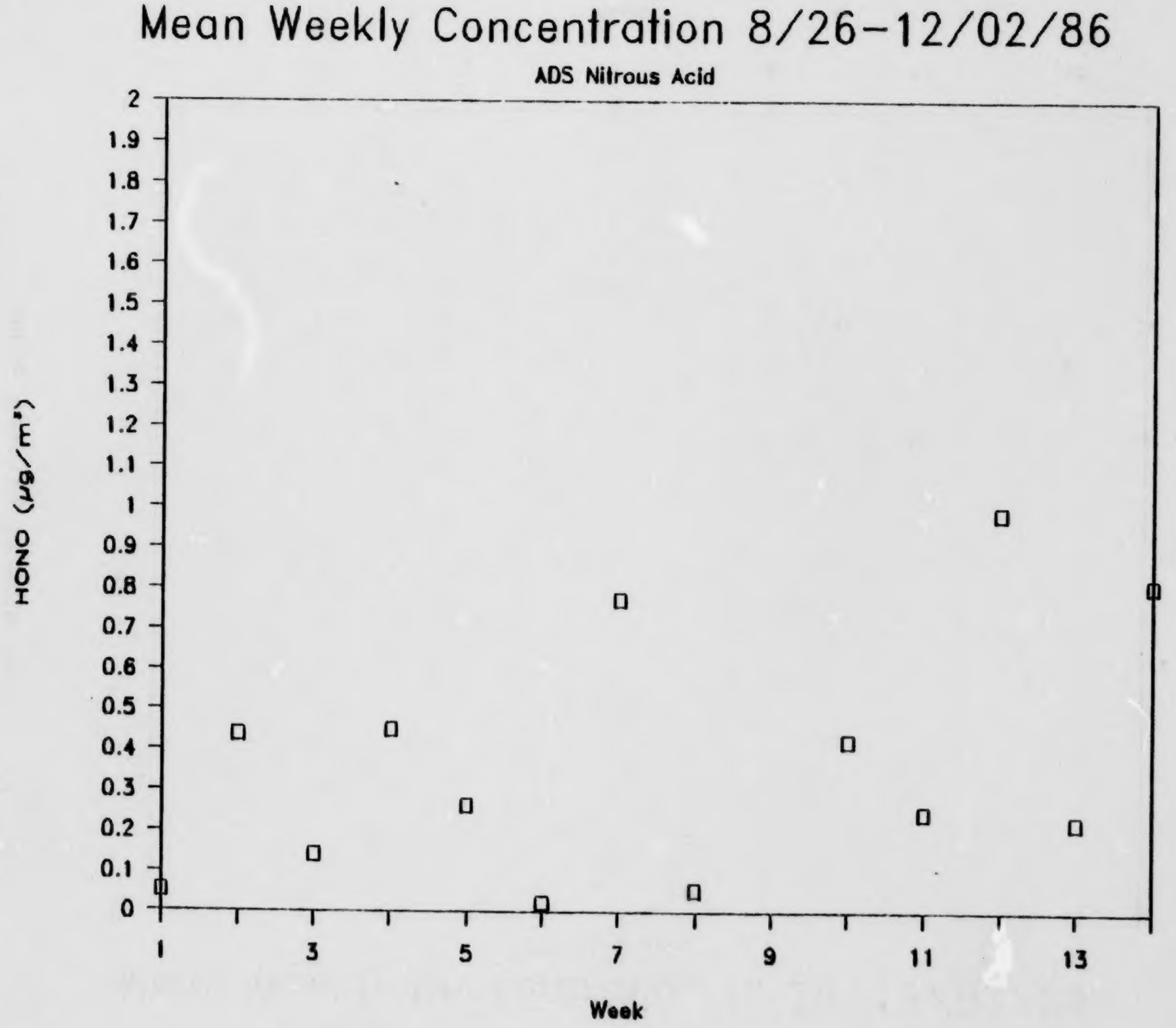


Figure 32. Mean weekly HONO concentrations from ADS sampler.

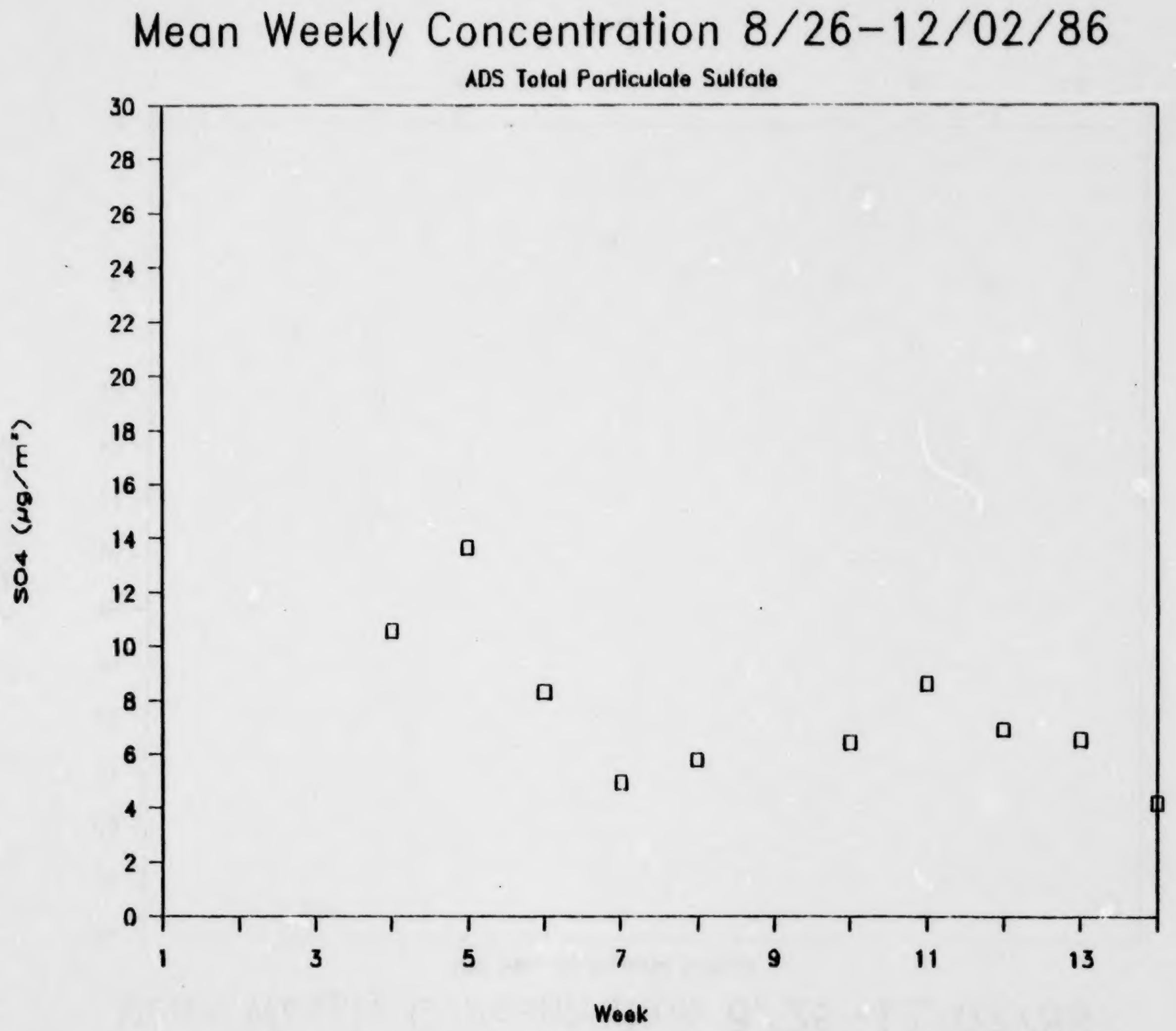


Figure 33: Mean weekly Total (particulate) SO_4^{2-} concentrations from ADS sampler.

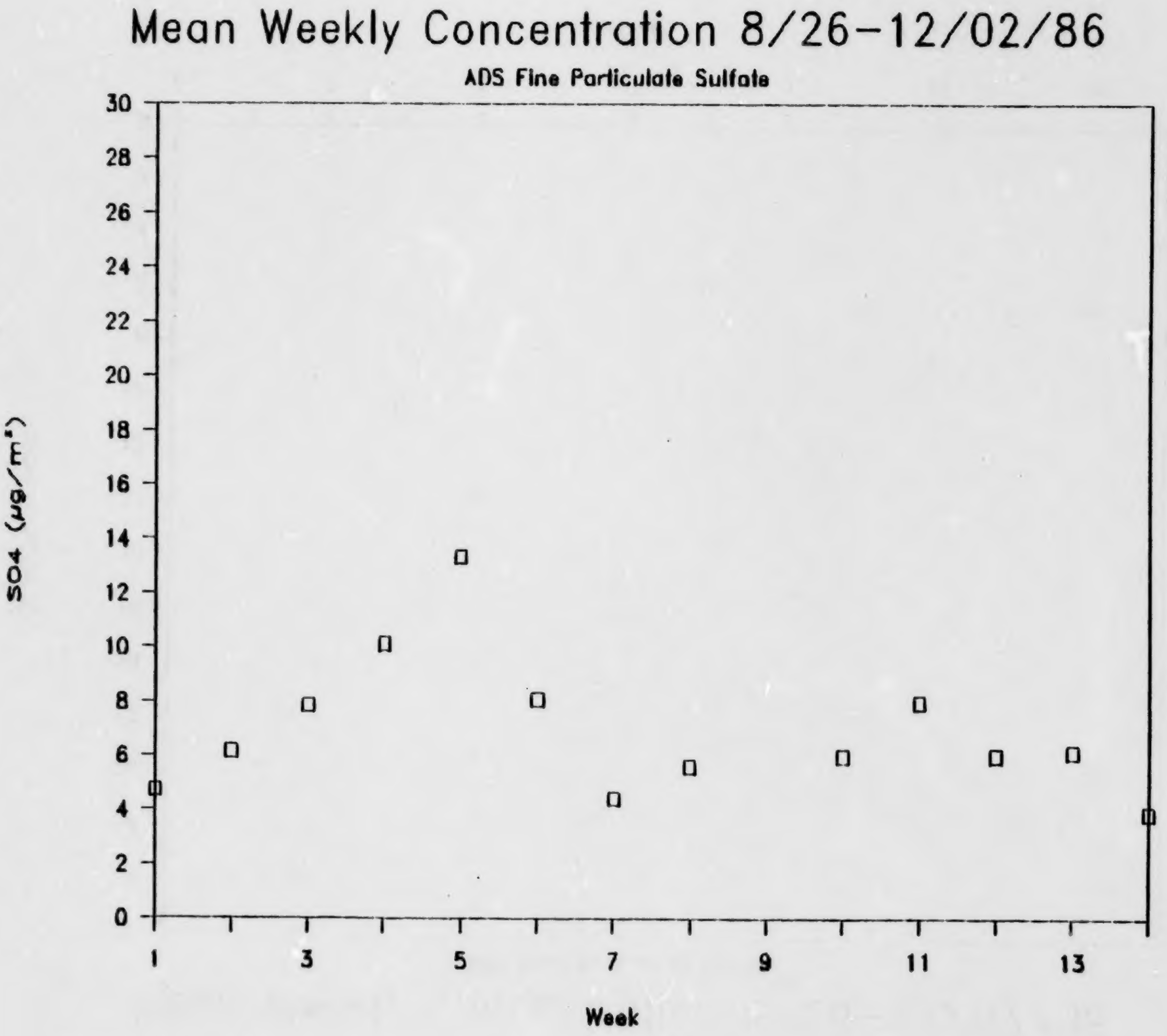


Figure 34. Mean weekly Fine (particulate) SO_4^{2-} concentrations from ADS sampler.

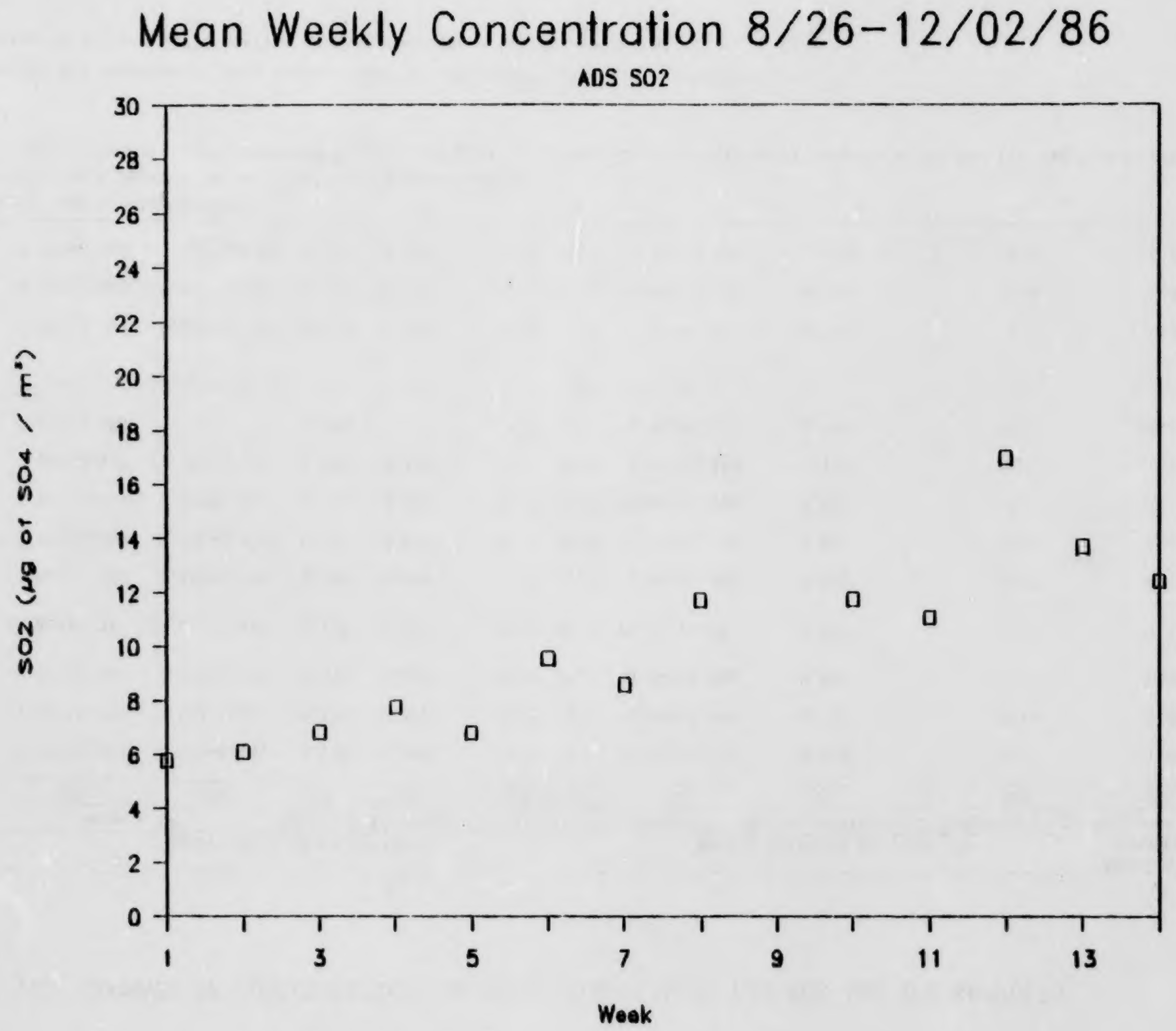


Figure 35. Mean weekly SO_2 concentrations from ADS sampler.

TABLE 18. SUMMARY OF CONCENTRATION AND PRECISION RESULTS FOR ADS AND TFR SAMPLERS

	Daily (9/29/86 to 10/12/86)						Weekly (8/26/86 to 12/02/86			Average Ratio Computed to Measured Weekly[c]
	Mean ± SD[a]		Median Difference[a,b]		Median CV,%		Mean±SD[a]	Median Difference[a,b]	Median CV,%	
	ADS	TFR	ADS	TFR	ADS	TFR	ADS	ADS	ADS	ADS
Total $NH_3+NH_4^+$	2.545±1.153	2.911±1.191	0.100	0.150	3.3	4.6	2.220±1.116	0.082	2.9	1.00
Fine NH_4^+	1.794±1.055	2.174±1.091	0.116	0.282	3.2	9.1	1.568±1.024	0.156	6.4	1.03
NH_3	0.717±0.246	0.632±0.176	0.111	0.115	10.0	13.5	0.388±0.208	0.064	13.4	0.96
H^+ Teflon	29.61±15.31[d]	22.82±16.74[d]	6.19[d]	6.86[d]	11.2	21.8	21.91±9.90[d]	1.44[d]	5.4	1.58
Total NO_3^-	3.086±0.586	3.141±0.739	0.189	0.055	4.2	1.3	3.946±0.360	0.120	2.3	0.79
Fine NO_3^-	0.602±0.559	-0.728±0.688[e]	0.105	0.513[e]	15.7	46.6[e]	0.688±0.255	0.037	4.4	0.88
NO_3^- Teflon	0.261±0.211	0.275±0.494	0.041	0.032	15.5	8.3	0.056±0.048	0.015	17.2	4.52
HNO_3	1.509±0.627	2.715±0.847	0.152	0.444	7.7	20.6	1.582±0.370	0.122	5.2	0.88
HNO_2	0.911±0.466	--	0.038	--	4.8	--	0.375±0.311	0.049	14.7	16.5[f]
NO_2	--	19.17±6.94	--	0.817	--	3.2	--	--	--	--
Total SO_4^{2-}	6.687±3.332	6.528±3.238	0.162	0.120	2.4	1.7	7.604±2.823	0.330	4.0	0.96
Fine SO_4^{2-}	6.275±3.446	5.972±3.282	0.183	0.120	2.2	1.9	6.955±2.569	0.262	2.9	0.95
SO_2 (as SO_4^{2-})	8.490±5.460	7.197±5.676	0.174	0.551	1.8	12.8	9.925±3.369	0.629	4.5	0.96

[a] Units: μg/m^3 except where noted otherwise.

[b] Median absolute difference between paired results of a given sampler.

[c] Average ratio of weekly concentrations computed from measured daily results to measured weekly results using ADS for two 1-week sampling periods.

[d] Units: n mol/m^3.

[e] TFR Fine NO_3^- results are negative in most cases. They do not permit meaningful comparisons.

[f] This is the average of 1.4 and 31.5; earlier studies have shown typical ratios of 1.2 to 3.4.

Ratios above or below unity for the remaining species suggest sample instability. The reason for the high ratio for H^+ Teflon is not clear. It may be reflecting a gradual loss by neutralization or volatilization of acidic species that is more important for 1-week samples than for 1-day samples. This observation is also consistent with the previously noted enhanced cation deficit in ion balances on weekly Teflon filter extracts. The difference may also be related to differences in precision associated with pH measurement for the daily and the more acidic weekly samples.

The ratio of computed to measured weekly results for HONO is thought to be high because collected nitrite is oxidized to nitrate to a larger extent in the ADS over the 1-week sampling duration than over 1-day periods. The low ratio for HNO_3 may also be reflecting this enhanced conversion of nitrite to nitrate in the weekly samples.

The high ratio for NO_3^- Teflon is likely the result of enhanced volatilization and loss of nitrate from the Teflon filter over the much longer 1-week sampling period than for the 1-day sampling periods. The sum of nitrate on the Teflon and nylon filters gives the Fine NO_3^-. Losses due to volatilization are considered in this case, and the ratio improves appreciably from 4.5 to 0.88. Nevertheless, the reason for this low ratio for Fine NO_3^- is unclear. The low ratio for Total NO_3^- reflects the combined low ratios for HNO_3, which can be reconciled, and for Fine NO_3^-, which cannot.

Statistical Analysis of ADS and TFR Results --

Correlation coefficients from linear regression analysis of ADS and TFR daily mean values for the 13-day study are given in Table 19. The average ratios of daily mean ADS to TFR results for each parameter are given in Table 19. Differences between the daily mean ADS and TFR values were used in t tests to determine if the two samplers give different results at the 95 percent confidence level. Results of these tests are also given in Table 19.

TABLE 19. COMPARISON OF ADS AND TFR RESULTS

	r[a]	Average Ratio of ADS to TFR[b]	t Test Results[c]
Total NO_3^-	0.96	1.00 ± 0.08	no difference
Fine NO_3^-	--	--	--
NO_3^- Teflon	0.18	1.83 ± 1.76	no difference
HNO_3	0.88	0.54 ± 0.12	ADS < TFR
HNO_2	--	--	--
NO_2	--	--	--
Total SO_4^{2-}	1.00	1.03 ± 0.04	no difference
Fine SO_4^{2-}	0.99	1.05 ± 0.06	ADS > TFR
SO_2	0.98	1.32 ± 0.30	ADS > TFR
Total NH_3 + NH_4^+	0.95	0.86 ± 0.13	ADS < TFR
Fine NH_4^+	0.95	0.79 ± 0.16	ADS < TFR
NH_3	0.49	1.17 ± 0.41	no difference
H^+ Teflon	0.86	1.59 ± 0.66	ADS > TFR

[a] Correlation coefficient for linear regression of mean daily ADS on TFR results, n = 13.

[b] Average of ratio of daily mean results for ADS and TFR (± one standard deviation).

[c] Results of t test for 13 paired results at 95 percent confidence level.

Behavior of Stable Species--Results of the ADS and TFR are highly correlated in most cases. In eight of 10 cases, correlation coefficients (r) exceed 0.85. For the two stable species, total particulate sulfate and total gaseous and particulate nitric acid and nitrate, the results from the two samplers are highly correlated, with average ratios of concentrations near unity. There is no apparent difference between the results from the two samplers. This provides strong evidence that both samplers were operating under known flow conditions. It also suggests that across-sampler differences in the partitioning of portions of the Total NO_3^- or Total SO_4^{2-} must depend on unique characteristics of the samplers employed.

Total NO_3^---As noted earlier, the measures of total gaseous nitric acid and particulate nitrate from the ADS and TFR are in agreement. They are highly correlated (i.e., $r = 0.96$). The average of the ADS to TFR ratios is 1.00±0.08, and the t test does not indicate a significant difference between the two measures.

Fine NO_3^---Calculations of TFR Fine NO_3^- using TFR theory resulted in negative values in 24 of 26 cases. The configuration of the TFR does not permit the direct determination of fine particle nitrate. However, a lower bound can be estimated. This estimate is the sum of the nitrate on the TFR Teflon filter and the difference between the nitrate found in the TFR and ADS cyclones. This estimate of Fine NO_3^- should be biased low by the amount of nitrate volatilized to the downstream nylon filter. If no volatilization occurs, then the estimate should be an accurate measure of Fine NO_3^- for the TFR. The ADS measure and the TFR estimate of Fine NO_3^- are highly correlated (i.e., $r = 0.93$) and exhibit an average ratio of 1.04±0.44 ($n = 12$). This indicates that on the average little particulate nitrate is lost from the Teflon filter in the TFR. It also suggests that the sum of the nitrate on the nylon strip and the nylon filter in the TFR may be used to estimate an upper bound for the gaseous nitric acid concentration.

NO_3^- Teflon--As noted previously, the nitrate remaining on the Teflon filter in the ADS and TFR cannot be compared directly. As a result, the poor correlation coefficient, 0.18, and the highly variable ADS/TFR ratio (i.e., SD = 1.76) are expected. The variability of the results prevents detection of a difference between the ADS and TFR measures of this parameter.

HNO_3--The ADS and TFR measures of HNO_3 are well correlated (i.e., r = 0.88). The average of the ADS to TFR ratios is 0.54±0.12, and the t test indicates that the difference between the measures is significant at the 95 percent confidence level. Using an approach discussed above, upper bound TFR HNO_3 estimates were made and compared to ADS measures of HNO_3. These parameters are highly correlated (i.e., r = 0.98), the average of the ADS to TFR ratios is 0.88±0.08, and the two measures are again significantly different at the 95 percent confidence level. These results show better agreement between TFR and ADS measures of HNO_3 when the TFR HNO_3 is computed under the assumption that the TFR functions similarly to a filter pack rather than according to TFR theory. These results also indicate that computation of TFR HNO_3 based on the sum of nitrate recovered from the nylon strip and filter can provide a useful upper bound for HNO_3 which can be used as a quality control parameter.

Total SO_4^{2-}--As noted previously, the measures of total particulate sulfate from the ADS and TFR are in agreement. They are highly correlated (i.e., r = 1.00), the average of the ADS to TFR ratios is 1.03 ±0.04, and the t test does not indicate a difference between the samplers.

Fine SO_4^{2-}--Although the fine particle sulfates are also highly correlated, for this parameter the ADS exceeds the TFR by approximately 5 percent, and the difference is significant at the 95 percent confidence level. This difference may be reflecting the difference in particle size cuts of the cyclones in the two samplers. The TFR cyclone with its smaller cut size removes more particulate mass than the ADS cyclone. As a result the ADS fine particle mass is expected to exceed that for the TFR, as observed. Since sulfates are dominantly in the fine particle size range, the observed discrepancy is not large. However, for the larger size particulate nitrates, the discrepancy is expected to be more pronounced.

$\underline{SO_2}$--The ADS and TFR measures of SO_2 are also highly correlated (i.e., $r = 0.98$). The average of the ADS to TFR ratios is 1.32 ± 0.30 (reciprocal = 0.76), and the t test indicates that the difference is significant. Tests of the recovery of SO_2 from TEA-coated filters conducted in our laboratory have shown approximately 80 percent recovery under humid conditions (see Appendix A). The observed discrepancy between the ADS and TFR SO_2 concentrations may be related to reduced sulfate recovery from the TEA-coated filters in the determination of SO_2 with the TFR.

$\underline{\text{Total } NH_3+NH_4^+}$--Total gaseous and particulate ammonium as measured by the ADS and TFR are highly correlated (i.e., $r = 0.95$). Although the average of the ADS to TFR ratios is 0.86 ± 0.13, the t test does indicate that the results of the two samplers are significantly different. A portion of this difference may be attributed to undersampling of particulate ammonium by the ADS since there was no provision in this sampler to collect any volatilized ammonium downstream of the Teflon filter. The average difference between the ADS and TFR is 0.366 ± 0.381 $\mu g/m^3$. If it is assumed that all the nitrate volatilized from the ADS (i.e., 0.341 $\mu g/m^3$) is accompanied by an equal molar amount of ammonium (i.e., 0.099 $\mu g/m^3$), then only 27 percent of the deficit can be accounted for as unsampled ammonium. The remainder is unreconciled, although it may result from NH_3 collected on hardware in the ADS that is not extracted and analyzed for ammonium.

$\underline{\text{Fine } NH_4^+}$--Fine particle ammonium measured by the ADS and TFR are highly correlated (i.e., $r = 0.95$). The average of the ADS to TFR ratios is 0.79 ± 0.16, and again the t test shows that the results of the two samplers are significantly different. While portions of the discrepancy may be attributed to undersampling of volatilized ammonium, (i.e. 0.099μg/m^3) and differences in cyclone efficiency (i.e. 0.072μg/m^3), they do not account for the total discrepency.

$\underline{NH_3}$--The ADS and TFR measures of ammonia are poorly correlated (i.e., $r = 0.49$), and the average of the ADS to TFR ratios is 1.17 ±0.41. The variability of the results prevents detection of a difference between the ADS and TFR measures of this parameter.

The above results suggest that the ADS undersamples the sum of gaseous and particulate ammonium, and that either the TFR or the ADS or both are not providing reliable measures of ammonia. More work is needed to permit a more complete understanding of the behavior of ammonia and ammonium in both the TFR and ADS samplers.

$\underline{H^+ \text{ Teflon}}$--Strong hydrogen ion is determined from the measured pH of the extract of Teflon filters in both the ADS and TFR. ADS and TFR measures of H^+ are well correlated (i.e., $r = 0.86$), and the average ratio is 1.59±0.66. In spite of the large variability, the t test indicates that the results of the two samplers are different at the 95 percent confidence level. The ADS H^+ concentration may exceed the corresponding TFR value in part because undenuded ammonia in the TFR neutralizes a portion of the H^+ in that sampler.

Comparison of Operational Features of TFR and ADS

Precision estimates for paired collocated sampling using the ADS and TFR as reported in several field studies are summarized in Table 20. These precision estimates show that both types of samplers provide results that generally agree to within ± 10 to 20 percent.

Studies designed to compare the performance of the TFR and the ADS were conducted by RTI during 1986. Technicians having no prior experience with either system were given the responsibility for set-up and operation of both systems. They were then asked to compile a list of "pros" and "cons" for each system. This information is summarized in Table 21: of the two, their preference from an operational standpoint was the ADS; although this preference was not strong. They were then asked to make suggestions that would facilitate the use of each system. Their suggestions are summarized in Table 22.

Relationships of Fine Particulate NH_4^+ and SO_4^{2-}

Data from four separate studies were examined to explore the relationships of fine particulate NH_4^+ and SO_4^{2-} in various environments. The data considered were collected in Los Angeles, CA during the late summer of 1985 and in the Research Triangle Park, NC in three separate studies during 1986. Sampling duration was 4 to 12 hours in LA and 22 hours to 7 days in NC. The three North Carolina studies were conducted during different seasons. The Spring Study was performed from 3/9/86 to 5/16/86; the Summer Study was performed from 7/7/86 to 9/16/86; and the Fall Study was comprised of daily samples from 9/29/86 to 10/12/86 and weekly samples from 8/26/86 to 12/2/86. The Summer and Fall Studies employed both ADS and TFR samplers. Graphical displays of NH_4^+ and SO_4^{2-} concentration data and their linear regressions are given in Figures 36 to 42. Results of linear regression analyses are given in Table 23.

Except for the Summer Study results, the NH_4^+ and SO_4^{2-} concentration data are highly correlated with correlation coefficients exceeding 0.85. Since the slope of the regression for the LA data exceeds 2.0, excess fine particle ammonium was present in this environment. For the RTP, NC data the regression slopes are less than 2.0.

TABLE 20. SUMMARY OF REPORTED PRECISION (MEDIAN CVs) FOR ADS AND TFR SAMPLER OPERATION IN SEVERAL FIELD STUDIES

	ADS						TFR	
	Fall 1985[a,b]		Spring 1986[b]	Fall 1986			Fall 1986	Fall 1984
Measure	4-6 hr	10-12 hr	22 hr	22 hr[b]	21 hr[c]	7-day[b]	22 hr[b]	7-day[d]
Total $NH_3+NH_4^+$	--	--	--	3.3	--	2.9	4.6	--
Fine NH_4^+	14.1	21.2	7.0	3.2	--	6.4	9.1	3.1
NH_3	19.5	--	17.9	10.0	--	13.4	13.5	--
H^+	--	--	--	11.2	--	5.4	21.8	--
Total NO_3^-	--	--	--	4.2	--	2.3	1.3	--
Fine NO_3^-	15.9	21.2	9.7	15.7	--	4.4	--	--
HNO_3	14.3	16.8	11.3	7.7	8.8	5.2	20.6	6.5
HNO_2	8.7	9.0	14.1	4.8	10.0	14.7	--	--
NO_2	--	--	--	--	--	--	3.5	8.8
Total SO_4^{2-}	--	--	--	2.4	--	4.0	1.7	--
Fine SO_4^{2-}	4.1	3.8	2.7	2.2	--	2.9	1.9	3.8
SO_2	8.0	5.8	8.8	1.8	3.7	4.5	12.8	3.7

[a] Reference 53.

[b] Based on results of tests conducted by RTI under the current contract.

[c] Reference 54.

[d] Reference 10.

TABLE 21. Positive and Negative Operational Features Associated with the ADS and TFR Systems

POSITIVE FEATURES

ADS	TFR
• Parts can be sealed and shipped	• Parts can be sealed and shipped
• Extractions performed in similar solutions using DI water except nylon filter where 0.003N NaOH is used	• All Teflon parts offer little chance for breakage
• Extraction volumes are same, 20 mL	• Filters can be prepared in advance, stored, and transported to the site
• Extractions can be completed in less than 1 hour	• Filters are easily distinguished by appearance
• Filters may be used directly without preparation	
• One flow rate to measure and maintain	
• Flow module is weatherproof	

NEGATIVE FEATURES

ADS	TFR
• Glass parts may be broken in handling	• Filters require different extraction procedure (i.e., solutions, volumes, and sonication times)
• Requires chemicals and equipment for preparing coating solutions and auxiliary gas for drying	• Cleaning procedure requires 1.5 hours
• Denuders need to be coated near the time of deployment and citric acid solution must be prepared daily	• Extraction requires > 2 hours of sonication
• Heating required to avoid condensation in denuders under humid conditions	• Preparation of filters (i.e., cutting, coating, and cleaning) is time consuming and complicated
• Denuders not easily distinguished by appearance: must be labeled	• Two or three flow rates to measure and maintain
• Teflon parts subject to excessive wear from routine use	• TEA-coated filters require operating temperatures above 5 °C to maintain good NO_2 collection efficiency
• Prone to leaks	• Teflon parts subject to excessive wear from routine use
	• Prone to leaks
	• Tylan flow controllers not designed for vacuum operations and offer marginal control at high filter loadings
	• Flow system requires weatherproof shelter

TABLE 22. SUMMARY OF SUGGESTIONS BY ADS AND TFR SYSTEM OPERATORS

Applicable System	Suggestion
Both	Color code and number each item (i.e., sampler, hoses, flow modules and assemblies). This will permit individual items of equipment to be associated with data artifacts.
Both	A pressure gauge should be installed between the filters and pump. This will permit checking for leaks and defective filters.
Both	Routine leak checks are recommended.
Both	Teflon joints deform after repeated use, permitting leaks. Redesign joints to eliminate problem.
Both	Quick connects to samplers and flow modules are essential. Stainless steel is preferable to avoid corrosion problems.
Both	Filters should be stamped, color coded, or otherwise marked to ensure correct assembly. Two potential problems exist: o mixing of nylon, Teflon, and/or other filters; and o reversal of Teflon (Zefluor) laminated PE-TFE membranes. Perhaps the PE side could be colored.
Both	Samplers should be prepared in a central facility and shipped sealed both to and from the sites (i.e., assembly and extraction done at central site). This has the following advantages: o greater uniformity between sites; o less chance for contamination at sites; o reduced site operator labor requirement; and o reduced site operator skill needed. Since many sites will be in remote areas where part-time operators will be used, the latter two advantages are very important. A major disadvantage will be the increase in equipment needed to provide for parts in transit. This requires that a sealable cap be designed for cyclones, and it also would make cyclone extraction (if desired) much easier.

TABLE 22. (continued)

Applicable System	Suggestion
Both	Use a screw-on cyclone shield; current ones often fall off in service.
Both	With the large number of sites proposed and the subsequent large number of samplers needed (at least two per site plus spares or more than 200 for a 100-site network), consideration should be given to injection molding Teflon parts from PFA rather than the current practice of machining them from TFE. This could provide greater uniformity as well as cost savings.
Both	The exact details of mounting ADS and TFR must be worked out before network start-up.
ADS	ADS denuder preparation requires individual instruction. A videotape should be prepared if individual instruction is not possible.
ADS	ADS denuders should be "keyed" so that misassembly and mismarking of samples is impossible (i.e., it should be physically impossible to interchange denuders 1, 2, and 3).
ADS	Filter Pack on ADS was difficult to close. Closer attention is needed in fabrication.
ADS	Hinge doors to sampler boxes so they can't fall off or become separated.
ADS	ADS thermostat should be redesigned to use temperature difference between box and outside air.
ADS	Denuders must be machined with flat, square edges, otherwise they won't seal properly.
ADS	Some type of flow-limiting drying rack should be designed for coating multiple denuders.
TFR	TFR strip "rolling" should be demonstrated to each preparer/operator by an experienced person. A videotape should be prepared if individual instruction is not possible.

TABLE 22. (continued)

Applicable System	Suggestion
TFR	The current TFR support is inadequate to prevent bending of apparatus in normal field use. Careful attention was needed to prevent bending, and this level of attention should not be expected in normal network use. Redesign the TFR support (this could include a splash guard; see next item).
TFR	A splash guard (rain shelter) should be designed for the samplers. This will: o keep rain out of inlets (--the present cyclone splash guard is inadequate); and o keep rain off joints and external parts and make handling and assembly easier.

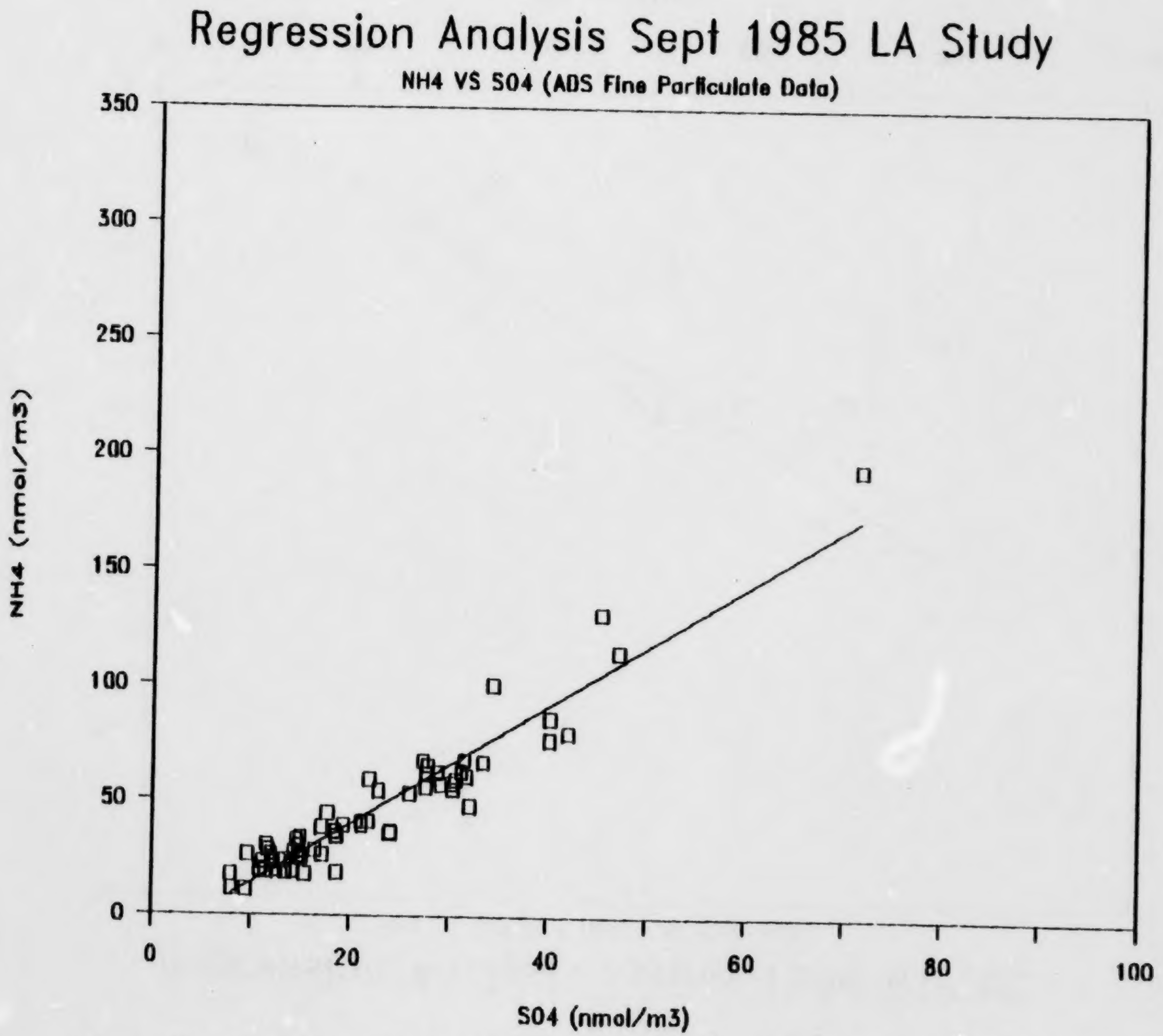


Figure 36. Comparison of Fine (particulate) NH_4^+ and SO_4^{2-} data collected in the September 1985 Los Angeles field study using ADS sampler.

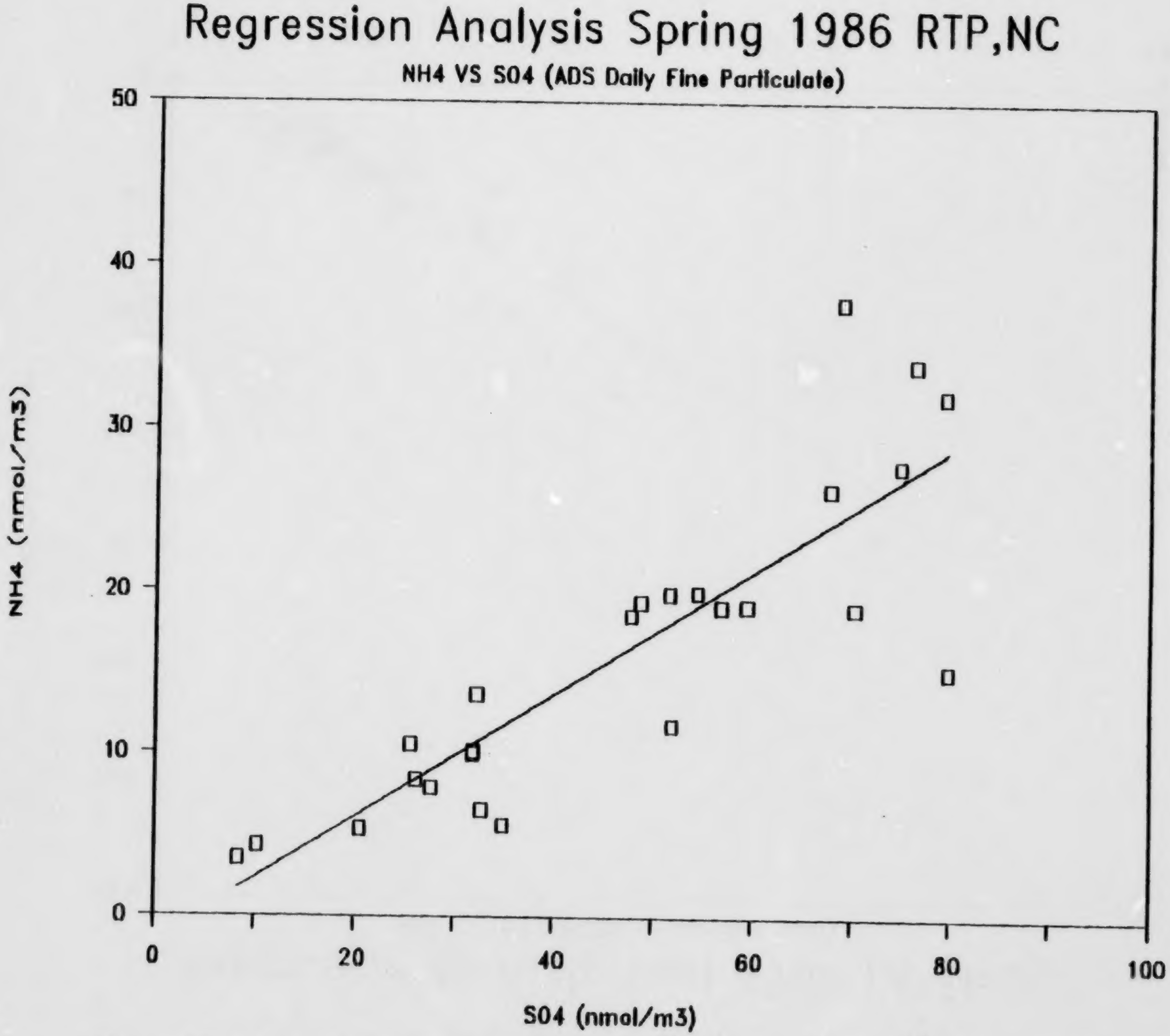


Figure 37. Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the spring of 1986 using ADS sampler.

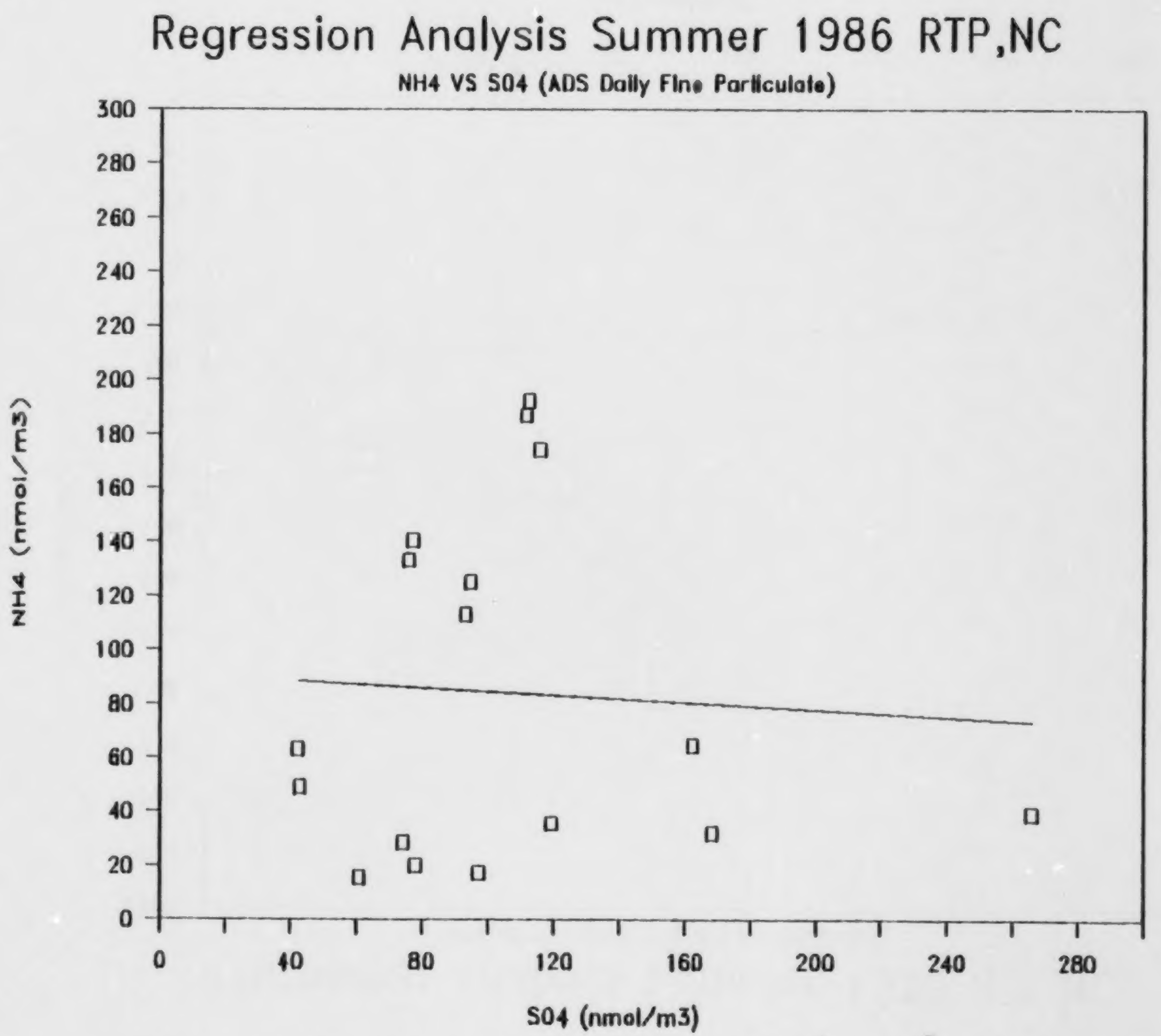


Figure 38. Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the summer of 1986 using ADS sampler.

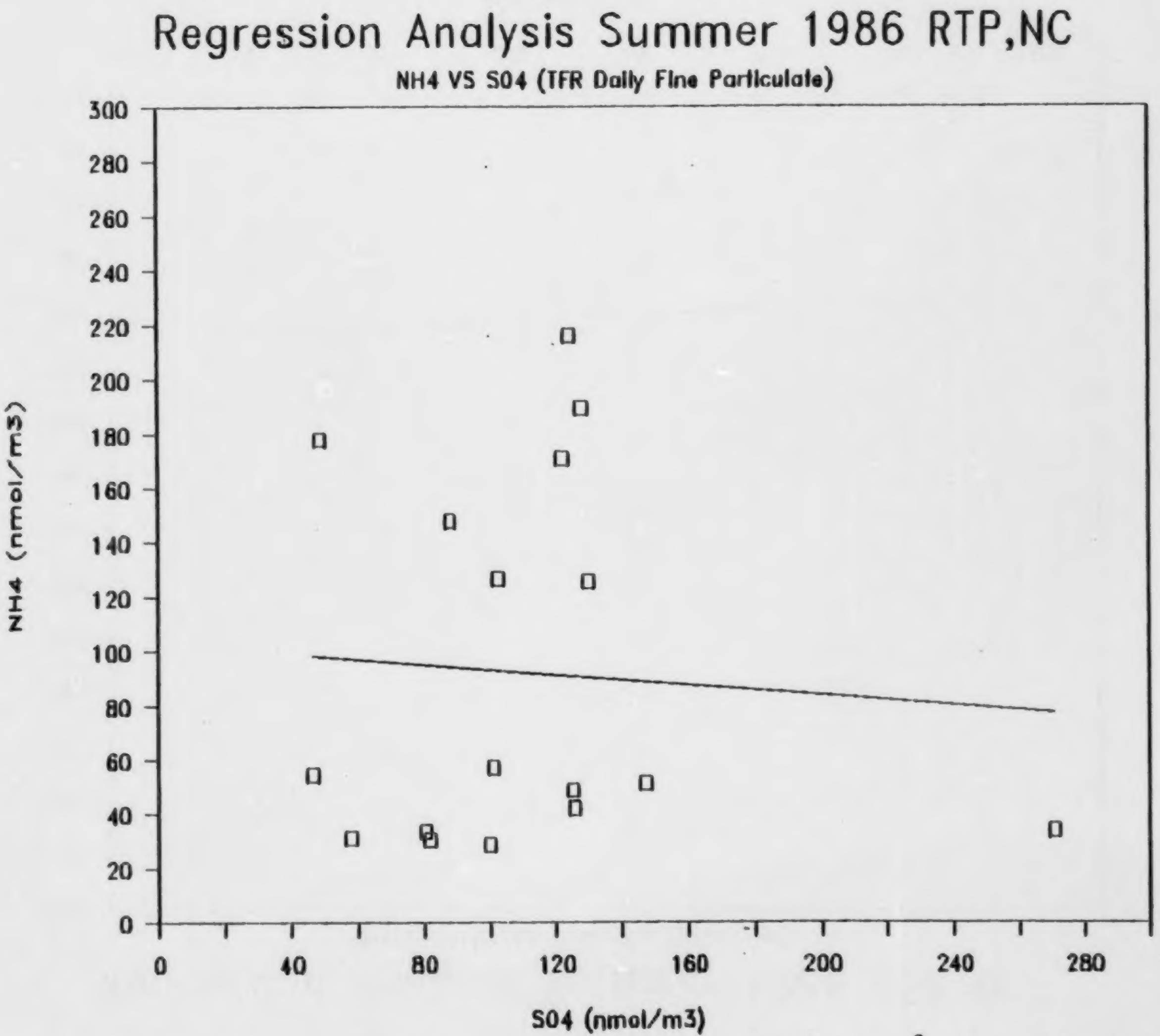


Figure 39. Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the summer of 1986 using TFR sampler.

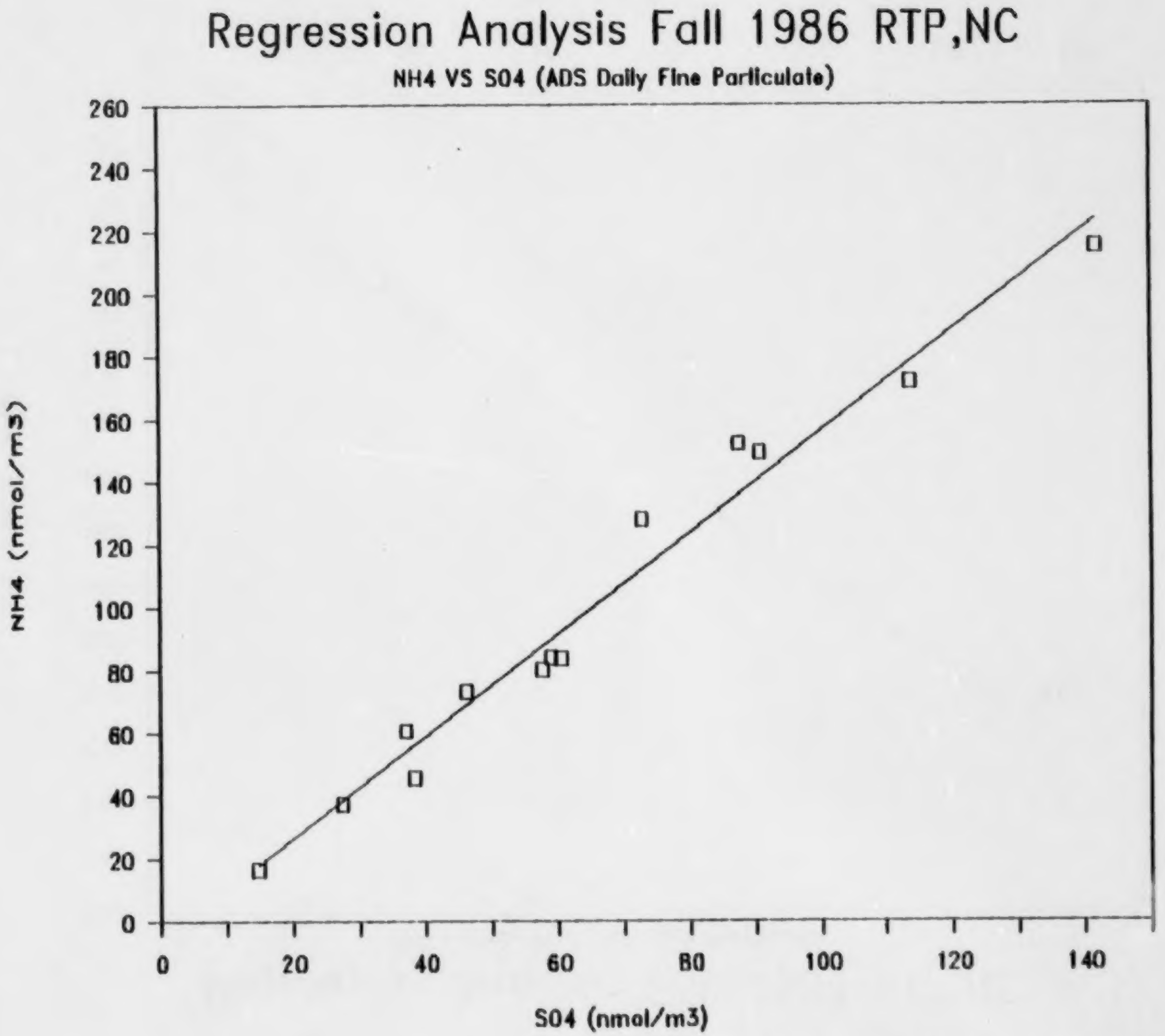


Figure 40. Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the fall of 1986 using ADS sampler.

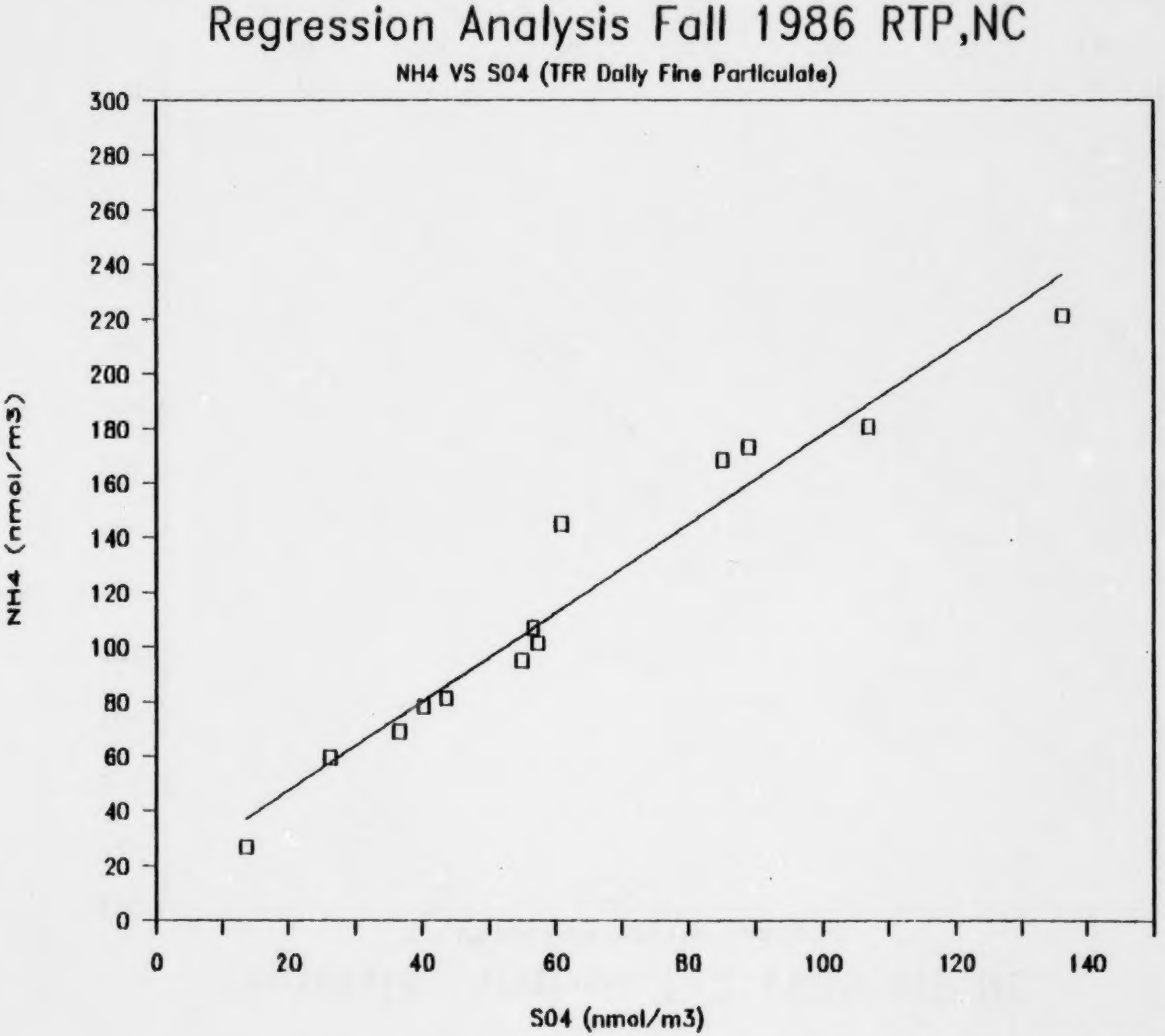


Figure 41. Comparison of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the fall of 1986 using TFR sampler.

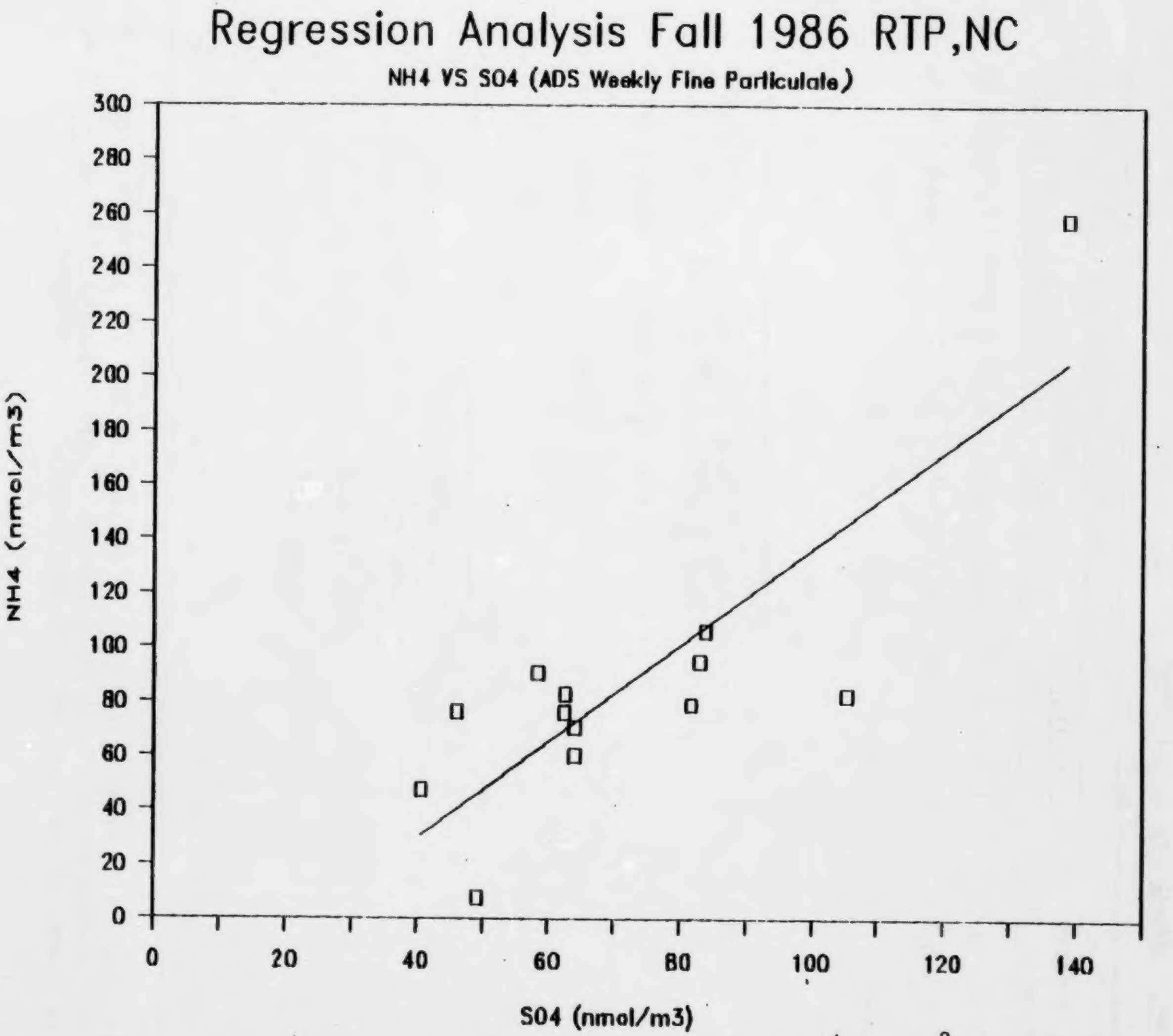


Figure 42. Comparison of weekly Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the fall of 1986 using ADS sampler.

TABLE 23. SUMMARY OF REGRESSION[a] ANALYSES OF NH_4^+ AND SO_4^{2-} DATA FROM FOUR FIELD STUDIES

	Los Angeles, CA September 1985	Research Triangle Park, NC 1986				
		Spring	Summer		Fall	
		Daily ADS	Daily ADS	Daily TFR	Daily ADS	Daily TFR
m	2.57 ± 0.11	0.38 ± 0.05	-0.07 ± 0.30	-0.09 ± -0.34	1.62 ± 0.08	1.62 ± 0.11
b	-11.5 ± 9.6	-1.46 ± 5.08	91.4	102.4	-5.69 ± 9.76	15.1 ± 13.4
r^2	0.91	0.73	0.00	0.01	0.97	0.95
n	62	25	17	17	13	13
			Before 9/3/86		Weekly ADS	
m			0.14 ± 0.08	0.03 ± 0.05	1.78 ± 0.35	
b			14.3 ± 13.9	33.8 ± 9.2	-41.6 ± 32.7	
r^2			0.34	0.05	0.70	
n			8	8	13	
			After 9/3/86			
m			1.67 ± 0.26	0.70 ± 0.60		
b			-11.0 ± 20.3	70.8 ± 54.9		
r^2			0.86	0.17		
n			9	9		

---

[a] Linear regression model: $y = mx + b$, where x is the SO_4^{2-}, y is the NH_4^+, m is the slope (± the standard error), b is the intercept (± the standard error of the y estimate), n is the number of samples, and r is the correlation coefficient.

This indicates that excess fine particulate sulfate was present at the North Carolina site and is consistent with the hypothesis of an acidic eastern aerosol.

The Summer Study results depicted in Figures 38 and 39 for the ADS and TFR both appear to be displaying results from two different populations. Those data generally falling above the regression lines were collected after 9/3/86, while those data generally falling below the regression lines were collected before 9/3/86. A composite plot of ADS data from the Spring, Summer, and Fall Studies is illustrated in Figure 43 and also suggests that two populations are present. Data collected in the spring and in the summer before 9/3/86 have regression slopes of less than 0.5. This indicates that during that period, fine particle sulfates were in substantial excess of fine particle ammonium and/or that sulfates other than $(NH_4)_2SO_4$ were present.

After 9/3/86 fine particle ammonium and sulfates approach stoichiometric proportions with sulfates remaining in slight excess. This relationship is maintained through the fall daily ADS and TFR studies and through the fall weekly ADS study. As shown in Figures 43 and 45 and in Table 23, the ADS daily and weekly comparisons are in general agreement. Both have similar regression slopes, 1.62 and 1.78. The weekly comparisons with an r^2 of 0.73 show more variability than the daily comparisons (i.e., $r^2 = 0.97$). As shown in Figures 38 to 41, comparisons from the ADS and TFR are in general agreement.

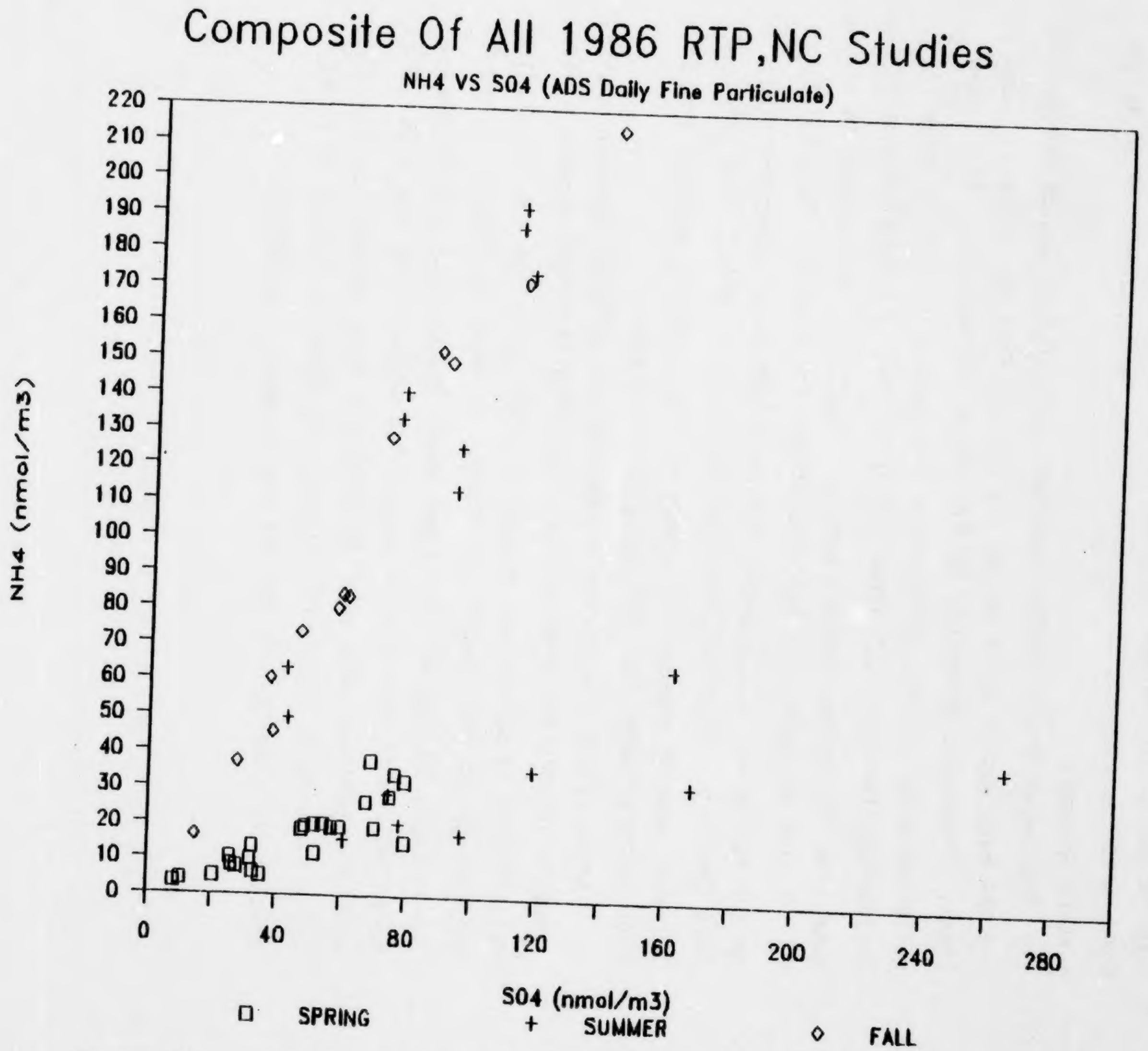


Figure 43. Composite of daily Fine (particulate) NH_4^+ and SO_4^{2-} data collected at RTP, NC in the spring, summer, and fall of 1986 using ADS sampler.

REFERENCES

1. Cox, K. W. and Sickles, J. E., II (1985). Sampling and Analysis Methods for Nitric Acid: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-04I.

2. Okita, T., Morimoto, S., Izawa, M., and Konno, S. (1976). Measurement of Gaseous and Particulate Nitrates in the Atmosphere. Atmos. Environ. 10: 1085-1089.

3. Appel, B. R., Wall, S. M., Tokiwa, Y., and Haik, M. (1980). Simultaneous Nitric Acid, Particulate Nitrate and Acidity Measurements in Ambient Air. Atmos. Environ. 14: 549-554.

4. Appel, B. R. (1986). Personal communication.

5. Mulawa, P. A. and Cadle, S. H. (1985). A Comparison of Nitric Acid and Particulate Nitrate Measurements by the Penetration and Denuder Difference Methods. Atmos. Environ. 19: 1317-1324.

6. Forrest, J., Spandau, D. J., Tanner, R. L., and Newman, L. (1982). Determination of Atmospheric Nitrate and Nitric Acid Employing a Diffusion Denuder with a Filter Pack. Atmos. Environ. 16: 1473-1485.

7. Anlauf, K. G., Wiebe, H. A., and Fellin, P. (1986). Characterization of Several Integrative Sampling Methods for Nitric Acid, Sulphur Dioxide, and Atmospheric Particulates. J. Air Pollut. Control Ass. 36: 717-723.

8. Wiebe, H. A. (1986). Personal communication.

9. Possanzini, M., Febo, A., and Liberti, A. (1983). New Design of a High-Performance Denuder for the Sampling of Atmospheric Pollutants. Atmos. Environ. 17: 2605-2610.

10. Knapp, K. T., Durham, J. L., and Ellestad, T. G. (1986). Pollutant Sampler for Measurements of Atmospheric Dry Deposition. Environ. Sci. Technol. 20: 633-637.

11. Sjodin, A. and Ferm, M. (1985). Measurements of Nitrous Acid in an Urban Area. Atmos. Environ. 19: 985-992.

12. Braman, R. S. and de la Cantera, M. A. (1986). Sublimation Sources for Nitrous Acid and Other Nitrogen Compounds in Air. Analyt. Chem. 58: 1533-1537.

13. Sanhueza, E., Plum, C. N., and Pitts, J. N., Jr. (1984). Positive Interference of Nitrous Acid. Atmos. Environ. 18: 1029-1031.

14. Mohnen, V. A. (1986). Personal communication.

REFERENCES (continued)

15. Winer, A. M., Peters, J. W., Smith, J. P., and Pitts, J. N., Jr. (1974). Response of Commercial Chemiluminescent NO-NO_2 Analyzers to Other Nitrogen-Containing Compounds. Environ. Sci. Technol. 8: 1118-1121.

16. Sickles, J. E., II and Grohse, P. M. (1984). Sampling and Analysis Methods for Sulfur Dioxide and Nitrogen Dioxide: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-01I.

17. Scintrex/Unisearch Technical Information Sheet on the LMA-3 (1986).

18. McClenny, W. A. (1986). Personal communication.

19. Stedman, D. H. (1986). Personal communication.

20. TECO Technical Information Sheet on the Model 43A (1986).

21. Forest, J. and Newman, L. (1973). Sampling and Analysis of Atmospheric Sulfur Compounds for Isotope Ratio Studies. Atmos. Environ. 7: 561-573.

22. Estes, E. D. and Sickles, J. E., II (1985). Sampling and Analysis Methods for Ammonia and Ammonium Ion: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-03I.

23. Stevens, R. K., Paur, R. J., Allegrini, I., DeSantis, F., Febo, A., Perrino, C., Possanzini, M., Cox, K. W., Estes, E. D., Turner, A. R., and Sickles, J. E. , II (1985). Measurement of HNO_3, SO_2, NH_3, and Particulate Nitrate with an Annular Denuder System. In Proceedings of Fifth Annual National Symposium on Recent Advances in the Measurement of Air Pollution. May 14-16, 1985. Raleigh, NC.

24. Kothny, E. L. (1973). Tentative Method of Analysis for Ammonia in the Atmosphere (Indophenol Method). Health Lab. Sci. 10: 115-118.

25. Eagan, M. L. and Dubois, L. (1974). The Determination of Ammonium Ion in Airborne Particulates with Selective Electrodes. Anal. Chem. Acta. 70: 157-167.

26. Mulik, J. D., Estes, E. D., and Sawicki, E. (1978). Ion Chromatographic Analysis of Ammonium Ion in Ambient Aerosols in Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor Science, pp. 41-51.

27. Wolff, G. T. (1984). On the Nature of Nitrate in Coarse Continental Aerosols. Atmos. Environ. 18: 977-981.

REFERENCES (continued)

28. Grohse, P. M. and Sickles, J. E., II (1985). Sampling and Analysis Methods for Sulfur Dioxide and Nitrogen Dioxide: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-02I.

29. Smith, J. P., Grosjean, D., and Pitts, J. N., Jr. (1978). Observation of Significant Losses of Particulate Nitrate and Ammonium from High Volume Glass Fiber Filter Samples Stored at Room Temperature. J. Air Pollut. Control. Ass. 28: 929-933.

30. Stevens, R. D. S. (1981). The Sampling and Analysis of Airborne Sulfates and Nitrates. Environment Canada Report No. EPS 5-AP-82-14.

31. Estes, E. D. and Sickles, J. E., II (1985). Sampling and Analysis Methods for pH and Acidity: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-05I.

32. McQuaker, N. R., Kluckner, P. D., and Sandberg, D. K. (1983). Chemical Analysis of Acid Precipitation: pH and Acidity Determinations. Environ. Sci. Technol. 17: 431-435.

33. Estes, E. D., Umana, M. X., and Sickles, J. E., II (1985). Sampling and Analysis Methods for Ozone: First Draft of a Literature Review. Research Triangle Institute Report No. RTI/2823/00-06I.

34. Martin, L. R. and Damschen, D. E. (1981). Aqueous Oxidation of Sulfur Dioxide at Low pH. Atmos. Environ. 15: 1615-1621.

35. Umana, M. X., Whitaker, D., and Sickles, J. E., II (1985). Sampling and Analysis Methods for Hydrogen Peroxide: First Draft of a Literature Review. Research Triangle Institute Report No. RTI/2823/00-09I.

36. Zika, R. G. and Saltzman, E. S. (1982). Interaction of Ozone and Hydrogen Peroxide in Water: Implications for Analysis of H_2O_2 in Air. Geophys. Res. Let. 9: 231-234.

37. Das, T. N., Moorthy, P. N., and Rao, K. N. (1983). Chemiluminescent Measurement of Atmospheric Hydrogen Peroxide in the Bombay Area. Atmos. Environ. 17: 79-82.

38. Schiff, H. I. and Mackay, G. I. (1984). Development of a Method for Measuring H_2O_2 in Real Air Using a Tunable Diode Laser Absorption Spectrometer. Electric Power Research Institute Report No. RP 2023-5.

39. Lazrus, A. L., Kok. G. L., Gitlin, S. N.. Lind, J. A., and McLaren, S. E. (1985). Automated Fluorometric Method for Hydrogen Peroxide in Atmospheric Precipitation. Analyt. Chem. 57: 917-922.

REFERENCES (continued)

40. Olszyna, K. J. (1986). Personal communication.

41. Dodge, M. C. (1986). Personal communication.

42. Vaeck, L. V., Cauwenberghe, K. V., and Janssens, J. (1984). The Gas-Particle Distribution of Organic Aerosol Constituents. *Atmos. Environ. 18*: 417-430.

43. Vaeck, L. V. and Cauwenberghe, K. V. (1978). Cascade Impactor Measurements of the Size Distribution of the Major Classes of Organic Pollutants in Atmospheric Particulate Matter. *Atmos. Environ. 12*: 2229-2239.

44. Farmer, J. C. and Dawson, G. A. (1982). Condensation Sampling of Soluble Atmospheric Trace Gases. *J. of Geophy. Res. 87*: 8931-8942.

45. Thomas, K. W., Sheldon, L. S., and Sickles, J. E., II (1985). Sampling and Analysis Methods for Organic Acids: First Draft of a Literature Review. Research Triangle Institute Report No. RTI/2823/00-07I.

46. Singh, H. B. and Salas, L. J. (1983). Methodology for the Analysis of Peroxyacetyl Nitrate (PAN) in the Unpolluted Atmosphere. *Atmos. Environ. 17*: 1507-1516.

47. Dasgupta, P. K., DeCesare, K. B., and Ullrey, J. C. (1980). Determiation of Atmospheric Sulfur Dioxide Without Tetrachloromercurate (II) and the Mechanism of the Schiff Reaction. *Analyt. Chem. 52*: 1912-1922.

48. Levin, J. O., Andersson, K., Lindahl, R., and Nilsson, C. A. (1985). Determination of Sub-Part-per-Million Levels of Formaldehyde in Air Using Active or Passive Sampling on 2,4-Dinitrophenlhydrazine-Coated Glass Fiber Filters and High-Performance Liquid Chromatography. *Analyt. Chem. 57*: 1032-1035.

49. Anlauf, K. G. (1986). Personal communication.

50. Mulligan, J. (1986). Personal communication.

51. Paur, R. J. (1986). Personal communication.

52. Ellestad, T. G. (1986). Personal communication.

53. Sickles, J. E., II, Perrino, C., Allegrini, I., Febo, A., Possanzini, M., and Paur, R. J. Performance and Results of the Annular Denuder System in the Sampling and Analysis of Ambient Air Near Los Angeles. In Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants. EPA Report No. 600/9-86-013, pp. 522-533.

REFERENCES (continued)

54. Stevens, R. K., Vossler, T. L., Paur, R. J., Baumgardner, R. E., and Bell, J. P. (1987). Inlets, Denuders and Filter Packs to Measure Acidic Inorganic Pollutants in the Atmosphere. Paper presented at ACGIH Advances in Air Sampling Symposium. February 1987. Pacific Grove, CA.

APPENDIX A

DEVELOPMENT OF A METHOD FOR THE SAMPLING AND ANALYSIS OF SO_2 AND NO_2 FROM AMBIENT AIR

The object of this effort was to identify and develop a method for the sampling and analysis of SO_2 and NO_2 from ambient air. Nominal concentrations range from 0.1 to 15 ppb. The ideal method would permit the simultaneous determination of both species with accuracy of ± 20 percent.

Both active and passive samplers were considered for development. Passive devices have several drawbacks including inaccuracies due to wind velocity effects in the absence of a diffusion barrier, inadequate testing of covered membrane samplers, requirement of calibration of membrane devices to compensate for wind velocity, temperature effects, and variability in membrane permeability, and accuracy of ± 20 percent at elevated workplace concentrations.

Active devices also have disadvantages. Bubblers present problems with handling, shipment, and limited sampling durations caused by evaporation. Uncoated and coated filters require careful storage and handling to avoid contamination. Uncoated and coated sorbents are easily stored and shipped but have sample flow limitations.

After evaluating the advantages of active and passive samplers, active samplers were chosen for further development. Assessment of the features of the various active samplers narrowed the focus of development efforts to coated sorbents and coated filters. The following sections describe the individual studies performed to arrive at a method for NO_2 and SO_2.

ALTERNATE NO_2 ABSORPTION SOLUTIONS

Screening tests of alternate absorption solutions (coating materials) were performed to measure their effectiveness at collecting NO_2. Several solutions were identified as likely candidates for NO_2 absorption from a literature review (1). Solutions were prepared

Preceding page blank

and evaluated in impingers by bubbling 0.4, 4.0, 200, and 2300 ppm NO_2 gas streams through 20 ml of solution for two hours. Nitrogen dioxide concentrations upstream and downstream of the impingers were determined using chemiluminescent NO_x monitors. Figures A-1 to A-4 show the absorption properties of each coating material as a function of time.

The best absorbent for NO_2 was a solution of 0.2M Na_2SO_3, 0.2M NaOH with $6x10^{-4}$ wt% Triton X-100 added. However, this coating solution is incompatible with IC analysis since the OH^- and SO_3^{2-} ions interfere with NO_2^- and SO_4^{2-} analyses. In addition, sulfite is readily oxidized by atmospheric oxygen, making it of marginal value for atmospheric sampling. Of the absorption solutions which may be analyzed via IC, the TEA solution exhibited the highest and most stable absorption (50-60%) of NO_2 from gas streams. TEA has also been reported to be an effective sorbent for SO_2 (1).

COLLECTION EFFICIENCIES OF COATED CHARCOAL AND FILTERS

A series of experiments to determine the collection efficiency for TEA-coated charcoal tubes and filters was conducted at various flow rates between 0.5 and 10 LPM. The tested filters were Whatman (glass fiber) GF/B, GF/C, GF/F, and (quartz fiber) QM-A. These tests were conducted with two coated filters in series. The experiments with charcoal tubes had only one tube in line.

These sampling devices were tested at 5°C, 25°C (ambient temperature), and 40°C, and were tested under both dry and humid (50 percent RH) conditions at each temperature. The nominal NO_2 and SO_2 concentrations delivered to each sampler in these tests were 160 and 130 ppb. Collection efficiencies were determined using a chemiluminescent NO_x monitor and a flame photometric SO_2 monitor to analyze the atmosphere upstream and downstream of each sampler.

Figure A-1 ALTERNATE COATINGS

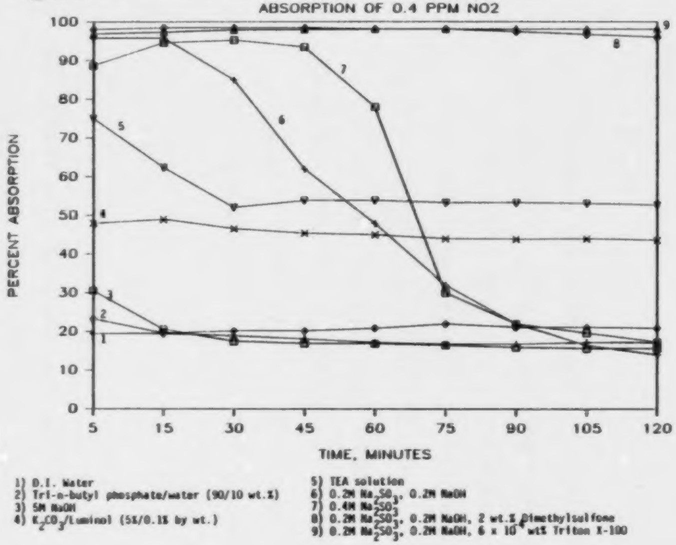

ABSORPTION OF 0.4 PPM NO2

Figure A-2 ALTERNATE COATINGS

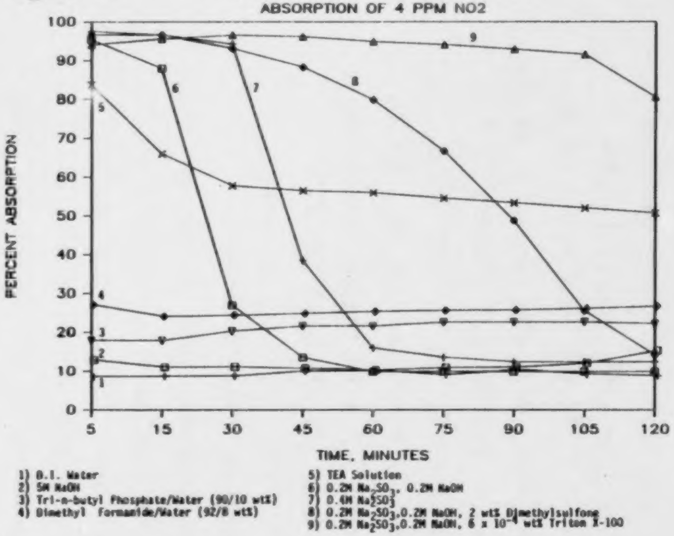

ABSORPTION OF 4 PPM NO2

Figure A-3 ALTERNATE COATINGS

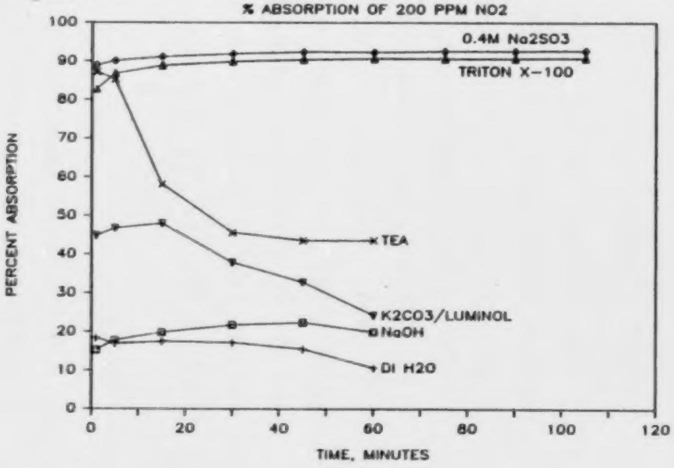
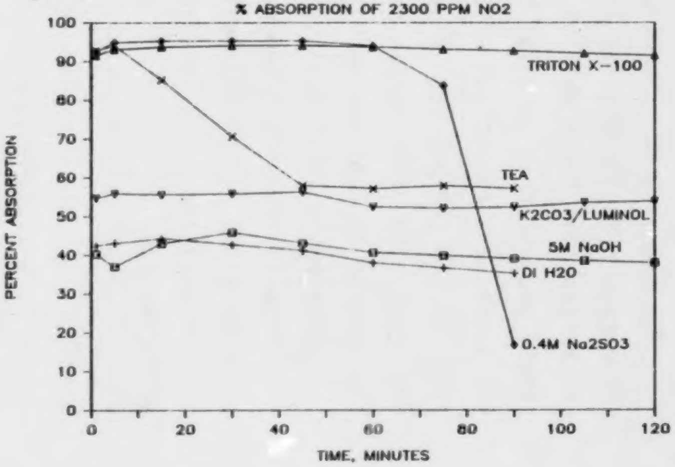

% ABSORPTION OF 200 PPM NO2

Figure A-4 ALTERNATE COATINGS


% ABSORPTION OF 2300 PPM NO2

The coated GF/B filters and charcoal tubes exhibited the highest collection efficiencies for NO_2. Collection efficiencies for the coated charcoal tubes at flow rates of 2.5 LPM and less were consistently greater than or equal to 92 percent. With the exception of the 5°C tests, the collection efficiencies of coated GF/B filters at flow rates of 1.5 LPM and less exceeded 90 percent. In the 5°C tests, the NO_2 collection efficiencies ranged from 78 to 90 percent at 1.5 LPM. The reduced NO_2 collection efficiency of TEA with reduced temperature is consistent with observations of others (2) and with the 21°C liquid-solid transition temperature for TEA. The SO_2 collection efficiency for all of the tests was greater than 95 percent.

In addition to the previously noted experiments at 160 ppb, tests were conducted at 40 and 340 ppb NO_2 to examine the influence of NO_2 concentration on collection efficiency. Tests were conducted with coated charcoal tubes sampling a dry atmosphere at 5°C, with coated GF/B filters sampling dry atmospheres at 5, 25, and 40°C, and with coated GF/B filters sampling a 25°C humid atmosphere. No differences in performance were apparent with flow rate at the three NO_2 levels that were studied.

ANALYTE LOADING

Experiments were performed to assess the precision of analyte loading operations. Four TEA-coated charcoal tubes were used simultaneously to sample a dry atmosphere containing a nominal 100 ppb NO_2 and SO_2. The recovered nitrogen determined as NO_2^- showed a CV (n=4) of 6.9%. This is consistent with the CV (n=4) of 10.3% displayed by the SO_4^{2-} data. Four pairs of TEA-coated filters were used in a similar experiment. In this case, the recovered NO_2^- showed a CV (n=4) of 8.3%, and the corresponding value for SO_4^{2-} was 9.4%. These experiments suggest that a precision of approximately 10% can be anticipated for loading NO_2 and SO_2 on filters or tubes.

STABILITY

A series of experiments was conducted to investigate the stability of collected NO_2 on TEA-coated charcoal and GF/B filters. In these experiments, four collectors were used simultaneously to sample a common atmosphere containing 50 to 100 ppb NO_2 for 16-18 hours at 1 LPM.

Subsequently, one sampler was flushed for 20 hours with clean air at 40°C, one at 27°C (room temperature), one at 5°C, and one was not flushed. The samples were then analyzed to determine the stability of the collected NO_2 and SO_2. Three sets of experiments were performed with each sampler type: sampling from a humid atmosphere and flushing with a dry atmosphere, sampling a dry atmosphere and flushing with a dry atmosphere, and sampling a humid atmosphere and flushing with a humid atmosphere.

In the tests with TEA-coated charcoal, the NO_2^- recovery decreased with increasing flush temperatures--on the average, only 37% of "no flush" NO_2^- could be accounted for under the "40° flush" condition. As the flush temperature increased, up to half of the collected NO_2 was converted to NO_3^-, and an increasing portion of the collected NO_2 was lost, presumably as gaseous NO and NO_2. The SO_4^{2-} recovery was generally less than 60 percent.

In the tests with TEA-coated GF/B filters, the NO_2^- recovery exceeded 90 percent and was essentially independent of flush temperature. Less than 15 percent of the collected NO_2 was converted to NO_3^-, and this portion was not associated with loading humidity or with flush temperature or humidity. The SO_4^{2-} recovery generally exceeded 75 percent.

These experiments indicate that coated GF/B filters are preferred for ambient sampling. As a result, subsequent tests were limited to TEA-coated Whatman GF/B filters. These filters are thick (0.73 mm), retain approximately 0.55 g of coating solution, and exhibit a pressure drop of 0.012 atm at 1 Lpm. Capacity studies revealed single-filter capacities of 100 µg NO_2/cm^2 and 200 to 400 µg SO_2/cm^2.

BLANK RESULTS

At low loadings, the level and variability of sulfur and nitrogen on the blanks may influence the apparent concentrations significantly. Coated and uncoated blank filters were washed with DI water or washed with aqueous KOH solution and extracted in DI water or IC buffer solution. Washing with DI water reduced blank SO_4^{2-} levels from 2 to approximately 1 µg/filter but had no appreciable effect on blank NO_2^- or NO_3^- levels. The additional effects of KOH washing, TEA coating, and extract solution on blank levels could not be distinguished. It should be noted that KOH washing resulted in disintegration of the filters and as a result, is not recommended. The mean (SD) background levels for NO_2^-, NO_3^-, and SO_4^{2-} on 22 DI-washed, TEA-coated GF/B filters are 0.87 (0.43), 0.66(0.24), and 1.13 (0.32) µg.

SPIKING EXPERIMENTS

Aliquots of standard solutions containing 50 µg/mL of NO_2^-, NO_3^-, and SO_4^{2-} were spiked with either TEA-coating solution or an equivalent volume of DI water and analyzed by IC. The presence of TEA did not influence the apparent species concentrations.

Standard solutions were added to DI water in polyethylene bags, DI water in Nalgene bottles, bags--each containing a coated filter and DI water, and bottles--each containing a coated filter and IC buffer. Recoveries in bags and bottles were greater than 95 percent, with those in bottles exceeding those in bags by an insignificant margin. No differences in recoveries were found between spiked coated filters in bagged samples of DI water and spiked coated filters in bottled samples of IC buffer. Spiked coated filters in bagged samples of DI water gave mean (SD) NO_2^-, NO_3^-, and SO_4^{2-} recoveries of 0.89(0.05), 0.95(0.06), and 0.90(0.03). This indicates that 5 to 10 percent of loaded NO_2^- and SO_4^{2-} may be retained by coated filters.

EXPERIMENTAL PROGRAM

An experimental program was designed to examine the influence of several variables on analyte recovery. The variables that were examined are species concentration in the sampled atmosphere, species loading, humidity, temperature, flushing, flushing temperature, and potential interferents. The results from NO_2 and SO_2 recovery tests performed under widely differing conditions are summarized in Table A-1. Each experiment was conducted using four sampling trains simultaneously to sample a common atmosphere.

Statistical Analysis

The results from the NO_2 and SO_2 recovery experiments were subjected to statistical analyses using an ANOVA on the reported mean recoveries adjusted for the unbalanced experimental design. Results showed no significant differences ($\alpha=0.1$) between recoveries obtained at high species concentrations and those at low species concentrations. Although there was a significantly ($\alpha=0.1$) lower NO_2 recovery at a species loading of 20 μg, it is based on three experiments conducted early in the program. The small sample size at 20 μg can argue for considering only the 10, 50, and 200 μg experiments. When results at these three loadings are considered, no significant differences ($\alpha=0.1$) are apparent among species recoveries obtained. Examination of the data for humidity effects showed no signifcant differences ($\alpha=0.1$) between NO_2 recoveries obtained at high and low levels. In contrast, there was a significant difference ($\alpha=0.05$) in SO_2 recovery associated with humidity. The mean SO_2 recovery under humid conditions was 80 ± 4% (n=10), while under dry conditions, it was 89 ± 6% (n=23).

Overall Analysis

On the average fractional recoveries are 0.87 ± 0.09 (n=32) for NO_2 and 0.86 ± 0.07 (n=33) for SO_2. The precision within any experiment is good showing an average standard deviation of 0.03 for NO_2 and 0.04 for SO_2. Examination of the distribution of collected nitrogen shows that most of the nitrogen is retained as nitrite: the average nitrate fraction is only 0.02. Most of the recovered nitrogen is found on the first filter: on the average 0.96. Sulfur dioxide is recovered as sulfate. Most of the recovered sulfate is found on the front filter: the average fraction is 0.99.

TABLE A-1. SUMMARY OF RESULTS FROM NO_2 AND SO_2 RECOVERY EXPERIMENTS

Species Concentration[a]	Species Loading, µg[b]	Loading		Flush		Humidity[c]	Interferent		Date	Recovery, Mean (SD)	
		Duration, hr	Temperature, °C	Duration, hr	Temperature, °C		Species	Loading, µg		NO_2	SO_2
H	20	0.33	30	--	--	D	--	--	10/24/84	75.0 (1.9)	89.1 (1.5)
H	50	1.0	30	--	--	D	--	--	10/24	81.8 (3.1)	87.9 (6.3)
H	50	1.0	30	--	--	D	--	--	10/24	80.3 (0.5)	--
H	50	1.0	30	--	--	D	--	--	10/24	--	89.8 (2.1)
L	10	0.83	30	--	--	D	--	--	10/25	86.3(12.4)	104.8 (4.1)
H	10	0.18	30	--	--	H	--	--	10/30	73.7 (4.6)	79.3 (3.3)
H	20	0.34	30	--	--	H	--	--	10/30	74.2 (3.0)	72.9 (1.5)
L	10	6.2	30	--	--	D	--	--	10/31	64.6((1.3)	77.0 (0.5)
H	10	0.17	30	17.8	30	D	--	--	11/01	69.4 (5.3)	86.7 (3.8)
H	200	3.4	30	17.8	30	D	--	--	11/01	79.4 (1.2)	92.1 (1.4)
H	50	0.85	30	--	--	H	--	--	11/01	88.3 (2.8)	83.3 (1.7)
L	20	2.4	30	--	--	D	--	--	11/02	79.9 (1.6)	97.1 (4.8)
H	10	0.17	30	--	--	D	--	--	12/11	90.1((3.7)	81.1 (4.2)
H	200	3.4	30	--	--	D	--	--	12/11	91.2 (3.9)	91.9 (4.2)
H	10	0.17	30	--	--	H	--	--	12/11	85.1 (1.4)	74.9 (2.4)
H	200	3.4	30	--	--	H	--	--	12/12	90.9 (0.8)	81.5 (1.5)
L	10	1.2	30	--	--	D	--	--	12/12	104.4(11.1)	83.6 (4.8)
L	50	5.7	30	--	--	D	--	--	12/13	86.6 (5.0)	80.3 (1.3)
L	200	23.0	30	--	--	D	--	--	12/13	82.4 (5.8)	82.8 (9.0)
L	200	23.0	30	--	--	H	--	--	12/18	97.6 (2.0)	77.8 (5.2)
L	10	1.2	30	--	--	H	--	--	12/19	92.6 (2.7)	83.7 (7.9)
H	50	0.87	30	--	--	D	--	--	12/20	101.7 (2.8)	87.3 (7.8)
H	50	0.87	30	17.3	30	D	--	--	12/20	91.2 (1.5)	94.4 (3.9)
H	50	0.87	40	--	--	D	--	--	12/21	93.5 (2.6)	94.6 (3.5)
H	50	0.87	30	19.8	40	D	--	--	01/04/85	92.7 (1.8)	94.5 (2.2)
H	50	0.88	30	17.0	5	D	--	--	01/07	88.6 (5.2)	91.8 (3.0)
H	50	0.87	5	--	--	D	--	--	01/08	81.6 (1.9)	87.8 (1.1)
H	50	0.87	30	--	--	D	NO	50	01/08	92.4 (3.9)	88.9 (5.6)
H	50	0.88	30	--	--	H	NO	50	01/09	97.6 (2.0)	81.3 (2.1)
H	50	0.88	30	--	--	D	NO	50	01/09	--	85.7 (1.4)
VL	50/90	48.8	30	--	--	H	--	--	01/14	91.4 (1.2)	86.0 (2.8)
VL	50/150	90.8	30	--	--	D	--	--	01/17	88.8 (2.1)	89.5 (4.3)
H	50	0.9	30	--	--	D	--	--	01/23	84.5 (1.4)	85.9 (2.7)
H	50	0.9	30	--	--	H	--	--	01/23	90.9 (2.4)	79.8 (3.1)
H	50	0.87	30	--	--	D	--	--	02/20	94.0 (--)	90.0 (--)
H	50	0.87	30	--	--	D	NH_3/S[d]	50	02/20	89.0 (--)	101.0 (--)
--	0	0	30	--	--	D	NH_3/S	50	02/20	0.00 (--)	0.01 (--)
H	50	1.0	30	--	--	H	O_3	50	03/11	86.3 (3.3)	--
H	50	1.0	30	--	--	H	NH_3/S	50	03/19	94.5 (1.0)	93.0 (1.8)
--	0	0	30	--	--	H	NH_3/S	50	03/19	0.00 (--)	0.02 (--)

---

[a] H = High concentration; nominal values: 400 ppb NO_2 and 200 ppb SO_2
L = Low concentrations; nominal values: 60 ppb NO_2 and 30 ppb SO_2
VL = Very low concentrations; nominal values 5 ppb NO_2 and SO_2

[b] Nominal Species Loadings

[c] D = Dry; H = Humid (50% RH)

[d] NH_3, CH_3SH, CS_2, H_2S each loaded to approximately 50 µg.

The following conclusions may be drawn from examination of the results in Table A-1.

- Variation in species concentrations in the sampled atmosphere ranging from 5 to 400 ppb does not lead to different recovery efficiencies.
- Recovery efficiency is relatively constant across species loadings ranging from 10 to 200 µg.
- NO_2 recovery efficiencies are not appreciably different at 0 and 50 percent relative humidity (RH); SO_2 recovery efficiency is reduced at 50 percent RH in comparison to that observed under dry conditions.
- Loading temperature ranging from 5 to 40°C does not exert an appreciable effect on species recovery except for NO_2 at 5°C; in this case, a small reduction in NO_2 recovery is indicated and the distribution of NO_2^- is shifted to the second filter.
- After loading at 30°C, flushing with clean air at temperatures from 5°C to 40°C has no apparent effect on the species recovery.

Interference Tests

The potential interference of several common atmospheric trace gases on the determination of NO_2 and SO_2 using TEA-coated filters was studied. The species considered are NO, O_3, NH_3, H_2S, CH_3SH, CS_2, PAN, and HONO. Results of tests of the first six potential interferents are summarized in Table A-1. Neither NO nor NH_3 interfere with NO_2 or SO_2 measurements. Ozone does not interfere with NO_2 determinations. The three tested sulfides show negligible interference with NO_2 or SO_2 measurements. Of the tested trace gases, however, both PAN and HONO were found to be major interferents.

PAN synthesized in iso-octane (3) was used to prepare air mixtures in bags ranging in concentration from 100 to 500 ppb as determined by chemiluminescence and by GC-EC. At PAN concentrations of 500 ppb, TEA-coated filters showed recoveries of 15 to 25 percent of the delivered PAN as NO_2^- and 55 to 70 percent as NO_3^-. Thus, PAN should be considered a significant interferent with the determination of ambient NO_2 using TEA-coated filters.

An HONO generator (4) was used to generate HONO concentrations ranging from 21 to 78 ppb as measured by chemiluminescence. The NO_2 atmosphere used in this study was at a concentration of 170 ppb. TEA-coated Whatman GF/B filters, Gelman nylon filters, Na_2CO_3-coated Whatman 41 filters, oxalic acid-coated Whatman 41 filters and Gelman Teflon filters were tested separately. The gas mixture upstream and downstream of each filter was analyzed using a TECO Model 14B NO_x analyzer, permitting estimates of collection efficiency by each filter type. Teflon and oxalic acid-coated filters failed to absorb either HONO or NO_2. The nylon filter appeared to absorb HONO up to a point and saturate at approximately 20 µg. This is consistent with reported findings using nylon wool (5). No NO_2 absorption was noted. Based on the chemiluminescent response, both the TEA-coated filters and the Na_2CO_3-coated filters absorbed all of the delivered HONO. The TEA-coated filter absorbed all the delivered NO_2, while the Na_2CO_3-coated filter absorbed only 4 percent of the NO_2. Since the absorbed HONO was recovered as NO_2^- by extraction and IC analysis of the TEA-coated filters, HONO may act as a significant interferent in the measurement of NO_2 using TEA-coated filters.

Results of the interference tests permit the following conclusions to be drawn:

- The presence of the potential interferents, NO, NH_3, O_3, H_2S, CH_3SH, and CS_2 have no apparent influence on species recoveries.
- PAN may act as a significant interferent.
- HONO may act as a significant interferent.

Comparison of K_2CO_3 and TEA-Coated Filters for SO_2 Collection

A filter preparation procedure using a coating of K_2CO_3 and glycerin on cellulose filters has been reported (6) and will be referred to as the Brookhaven Method. This method uses S&S No. 2 FF (cellulose) filters. TEA-coated Whatman GF/B glass fiber filters were used for comparison. The S&S filter is thin and offers very low resistance to gas flow in comparison to the Whatman 41 (cellulose) and GF/B filters.

Results of laboratory and ambient studies show a single Brookhaven filter to have slightly lower SO_2 collection efficiency than a single TEA-coated filter. In practice, two Brookhaven filters are used in series. This seems justified based on their reduced single-filter efficiency. Two K_2CO_3-glycerin-coated Whatman 41 filters are employed to collect SO_2 in the Environment Canada acid deposition monitoring network. It is likely that the SO_2 collection efficiency using this approach is at least equivalent to that using two Brookhaven filters.

REFERENCES

1. Sickles, J. E., II and Grohse, P. M. (1984) Sampling and Analysis Methods for Sulfur Dioxide and Nitrogen Dioxide: A Literature Review. Research Triangle Institute Report No. RTI/2823/00-01I.

2. Girman, J. R., Hodgson, A. T., Robinson, B. K., and Traynor, G. W. (1984). Laboratory Studies of the Temperature Dependence of the Palmes NO_2 Passive Sampler. In Proceedings of the National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources. EPA Report No. 600/9-84-001, pp. 152-166.

3. Holdren, M. W. and Spicer, C. W. (1984) Field Compatible Calibration Procedure for Peroxyacetyl Nitrate. Environ. Sci. Technol. 18: 113-116.

4. Braman, R. S. and de la Cantera, M. A. (1986) Sublimation Sources for Nitrous Acid and Other Nitrogen Compounds in Air. Analyt. Chem. 58: 1533-1537.

5. Sanhueza, E., Plum, C. N., and Pitts, J. N., Jr. (1984) Positive Interference of Nitrous Acid. Atmos. Environ. 18: 1029-1031.

6. Daum, P. H. and Leahy, D. F. (1982) The Brookhaven National Laboratory Filter Pack System for Collection and Determination of Air Pollutants. Report by Brookhaven National Laboratory. Upton, NY 11973.

APPENDIX B

LABORATORY TESTING OF ANNULAR DENUDERS AND NYLON FILTERS

SUMMARY

Annular denuders were tested to investigate the recovery efficiency of three coatings for NO_2 and SO_2 under various laboratory conditions. The coating formulations are identified in Table B-1. Both sodium carbonate (Na_2CO_3) and triethanolamine (TEA) coating solutions, showed recoveries above 85% when tested with SO_2. Recoveries of NO_2 and PAN from the Na_2CO_3 coating solutions were low at 1 and 3 percent. When tested with NO_2, TEA displayed a less than 25 percent recovery. The recovery of NO_2 with potassium iodide, sodium arsenite ($KI-NaAsO_2$) coating solution increased with humidity. The recovery of PAN from the $KI-NaAsO_2$ solution also increased with humidity and averaged 10 percent.

EXPERIMENTAL

Annular denuders were connected to a glass inlet manifold with Teflon fittings. The flow was maintained through each denuder at 5 Lpm with a mass flow controller. This arrangement permitted the gas to be sampled directly from the inlet manifold and after passing through the denuder by either a Bendix 8101B NO_x Analyzer or a Monitor Labs 8450 SO_2 Analyzer. This approach permitted comparison of the actual strip chart recording of the fraction of pollutant absorbed (collection efficiency) with the analytical fractional recovery.

The NO_2 atmosphere was generated with a permeation tube; while the source of the SO_2 was a calibrated gas cylinder. The analytical recovery was determined by ion chromatography (IC) for the Na_2CO_3 and TEA coatings. A colorimetric technique was used for the determination of NO_2^- in the $KI-NaAsO_2$ solutions.

Preceding page blank

TABLE B-1. DENUDER COATING FORMULATIONS

Na_2CO_3	1.0g Sodium Carbonate 1.0g Glycerol 40.0 ml Deionized Water 60.0 ml Methanol
$KI\text{-}NaAsO_2$	10.0 g Potassium Iodide 1.0 g Sodium Arsenite 5.0 g Ethylene Glycol 25.0 ml Deionized Water 75.0 ml Methanol
TEA	22.3% v/v Triethanol Amine 3.6% v/v Ethylene Glycol 50.0% v/v Acetone 24.1% v/v Deionized Water

RECOVERY OF THREE COATING FORMULATIONS

SO_2 is effectively absorbed by annular denuders with either a Na_2CO_3 or a TEA coating solution. At all humidity conditions the recovery was above 85%. When two denuders were connected in series, 99% of the total was recovered from the front denuder.

The IC analysis showed SO_2 to be captured as SO_3^{2-} under laboratory conditions. The addition of an oxidizing agent was required to convert SO_3^{2-} to SO_4^{2-}. Two drops of 30% hydrogen peroxide (H_2O_2) per 10 ml extract were found to be sufficient.

The recovery efficiency of NO_2 using KI-$NaAsO_2$-coated annular denuders is humidity dependant. Under dry conditions the recovery was 19%, at 20% RH the recovery was 17%, at 40% RH the recovery was 25%, while at 70% RH the recovery was 90% based on colorimetric analysis for NO_2^-.

The recovery efficiency of NO_2 using the TEA-coated annular denuders is 10% under dry conditions and 22% at 70% RH.

The experimental design permitted on-line recording of the extent of NO_2 or SO_2 absorption by the denuders. Results of the Monitor Labs SO_2 analyzer agreed with the IC results for Na_2CO_3- and TEA-coated denuders. The Bendix NO_x analyzer showed absorption values close to those obtained by IC for both the TEA-coated and KI-$NaAsO_2$-coated denuders.

PAN INTERFERENCE

A study was also conducted to determine the extent of peroxyacetyl nitrate (PAN) interference on the recovery of NO_2. KI-$NaAsO_2$- and Na_2CO_3-coated denuders were tested with both dry and humid PAN and NO_2-PAN gas mixtures. The PAN concentrations were 100 to 500 ppb as analyzed by both chemiluminescence (CLM) and gas chromatography using an electron capture detector. The NO_2 concentration as determined by CLM was 200-300 ppb.

The PAN was synthesized in a solution of iso-octane. The PAN iso-octane mixture and the NO_2 were introduced into a 130 liter Teflon bag through a septum while diluting the contents with zero air.

The bagged sample was then drawn through the denuders with a pump. The denuders were subsequently extracted and analyzed by IC (Na_2CO_3-coated denuders) for NO_2^- and NO_3^- or by colorimetry ($KI-NaAsO_2$-coated denuders) for NO_2^-.

The Na_2CO_3-coated denuders had an average recovery of 2.1 percent of PAN as nitrite, with 0.8 percent as nitrate. The Na_2CO_3 coating displayed a mean NO_2 recovery of 1.1 percent as nitrite with no detectable amount as nitrate.

An average of 10 percent of the PAN was recovered as nitrite from $KI-NaAsO_2$-coated denuders. Under dry conditions, approximately 6 percent of the PAN was recovered as NO_2^-. This increased to 16 percent under humid conditions.

NITRATE RECOVERY FROM NYLON FILTERS

A comparison study of extraction methods was conducted for nylon filters. Gelman nylon filters, 47 mm diameter 1 µm pore size, were spiked with 100 µl of a solution of 200 µg/ml KNO_3 and 200 µg/ml K_2SO_4. These filters were then extracted with 20 ml of solution and sonicated for 20 minutes at either 70°C with deionized water, 25°C with deionized water or 25°C with 0.003 N NaOH. Ion chromatography was used for NO_3^- and SO_4^{2-} determination immediately after extraction, after two hours, and after four hours. The pH was simultaneously monitored. A repeat of the test was performed with the addition of wetting solution containing 0.1% Photo-Flo 200 (Kodak) and 0.15% polyvinylpyrrolidone.

The recovery results remained constant throughout the time frame of the study. No decline in NO_3^- was recorded. This is in contrast to the results of spiked filters in the September 1985 L.A. study. The use of the wetting solution did not alter NO_3^- or SO_4^{2-} extraction efficiencies.

Test results indicate that 0.003 N NaOH was more efficient in desorbing the NO_3^- and SO_4^{2-} from the nylon filters than deionized water at 25° or 70°C. In three cases, the pH of the 25°C water extract was raised from 6 to 11 with NaOH, and the NO_3^- and SO_4^{2-} recoveries increased by 29 and 14%. Four samples that were initially extracted at 70°C in deionized water at a pH of 6 did not show an appreciable change in recovery upon NaOH addition.

APPENDIX C

PROTOCOL FOR THE ANNULAR DENUDER SYSTEM:

DETERMINATION OF ATMOSPHERIC CONCENTRATIONS OF GASEOUS HONO, HNO_3, SO_2, AND NH_3, OF FINE PARTICULATE NITRATE, SULFATE, AND AMMONIUM, OF HYDROGEN ION, AND OF VOLATILE NITRATE

PURPOSE

To sample dry deposition constituents for periods of hours to 7 days for concentration determination of gaseous HONO, HNO_3, SO_2, and NH_3, and of fine particulate NO_3^-, SO_4^{2-}, NH_4^+, and H^+. Accuracy goals are ± 15 percent.

METHOD

Air is drawn at a nominal sampling rate of 15 Lpm through a Teflon cyclone to remove particles larger than about 3.3 μm (D_{50} where ρ = 1.0). The air then passes through two annular denuders for collection of HONO, HNO_3, and SO_2, followed by a third annular denuder for collection of NH_3. The air then passes through a filter pack containing a Teflon and a nylon filter for collection of fine particulates and volatile nitrate.

In the annular denuders, ambient air is passed under laminar flow conditions through the annular space of two concentric tubes. The outside of the inner tube and the inside of the outer tube are coated with a specific gas-absorbing solution. For the first two denuders, this solution contains Na_2CO_3; for the third denuder, the NH_3-absorbing solution contains citric acid. The third denuder is followed by a Teflon filter to collect particulate sulfate, nonvolatilized nitrates, and particulate ammonium, while the nylon filter collects HNO_3 that is passed due to volatilization from the Teflon filter.

The samples are extracted according to their specific protocols and analyzed by ion chromatography, specific ion electrode, or colorimetric techniques, as appropriate. The average species concentrations are calculated from the analysis of the extracts and the sampler flow data.

OPERATIONS PROTOCOL

Plastic gloves should be worn when handling denuders, filters, and equipment. The workspace should be clean. Use a large Kimwipe underneath the filter pack when assembling and removing filters. While assembling, minimize time that filters are exposed in the laboratory. Avoid breathing directly on denuders or filters. Smoking shall be prohibited in any areas used for sampler preparation, analysis. or storage. Keep denuders capped when not assembled.

A. Preparation of Na_2CO_3 and citric acid coated denuders:

Follow the attached protocols for preparation.

B. Loading of filters into filter holders:

Using tweezers, load the nylon and Teflon filters into the filter pack, as shown in Figure C-1. Either side may go up for the nylon filter. The suede side of the Teflon filter must go up--this is the side which is facing up in the box supplied by Gelman. Reassemble and firmly tighten the filter pack.

C. Assembly of ADS into sample box:

1. Put the cyclone in position with the inlet facing up to the open side of the box. Slide the aluminum shield into place over the cyclone and the bottom of the box.
2. Remove caps from first Na_2CO_3 denuder. Firmly screw one end into the cyclone and one end to a coupling. The second Na_2CO_3 denuder screws into the coupling following the first. Attach a coupling to the other end of the second denuder. The citric acid denuder screws into the coupling with the second denuder and also into the filter pack. Position sample flow line into the bottom of the filter pack, making sure the fit is snug. Use Velcro to hold ADS in place on bracket. Attach a min/max thermometer inside of sample box (Figure C-2).

Set-Up

A. Assemble the apparatus inside of the sample box. Leak check and tighten so no leaks remain. Latch the lid on securely.

B. Mount at the predetermined site. Connect flow and electrical connections to sample box. Turn on flow module, recording date, time, rotameter, and vacuum settings.

C. Measure the actual flow at the beginning and end of sampling periods. This can be done by connecting a dry gas meter in line with the inlet side connected to the ADS and the out side connected to the input of the flow module (see Figure C-3) (quick-connects simplify the connections). Using a decimal minute stopwatch, record the time for a 20 standard L volume. Measure the time required for two additional samples. Record all three times. Record the pressure drop and temperature from gauges on the dry gas meter.

D. Record date and time of system shutoff.

ANNULAR DENUDER PROTOCOL

A. Cleaning of denuders

1. New: Soak in soapy water 30 minutes. Flush with tap water. Use deionized water to half-fill; cap, shake, and empty. Repeat deionized water rinse two more times. Fill 1/4 of denuder with acetone; shake and empty. Dry with zero air. Recap.

2. Used: a) Omit soap and tap water steps. Use deionized water rinses and an acetone final rinse. Dry with zero air. Recap.

   b) After every four uses, repeat step 1.

B. Coating solution

1. Na_2CO_3. Dissolve 1 g Na_2CO_3 in 40 ml deionized H_2O; add 1 g glycerol and dilute to 100 ml with methanol. Cap flask.

2. Citric Acid. Dissolve 1 g citric acid in 100 ml methanol. Cap flask. This solution should be made fresh daily.

C. Coating

Remove one cap from the denuder and pour about 10 ml of the coating solution into the clean dry annular space of the denuder. Recap the denuder and swirl gently to make sure that all surfaces are wetted. Decant off excess solution and gently dry with a zero air line while rotating to ensure an even coating. CAUTION: Excessive air flow during drying will blow coating off denuder walls.

D. Extraction

Cap one end and pipette in 10 ml of deionized water. Recap open end and shake for 1 min, making sure all surfaces are wetted. Decant off into a clean sample bottle. Pipette in a second 10 ml aliquot of deionized water and repeat procedure.

Two drops of 30 percent H_2O_2 should be added to the Na_2CO_3 denuder extracts to ensure conversion of SO_3^{2-} to SO_4^{2-}.

E. Analysis

Analyze the Na_2CO_3 extracts by ion chromatography for NO_2^-, NO_3^-, and SO_4^{2-}. Analyze the citric acid extract by colorimetric techniques (Indophenol blue) for NH_4^+. Prior to analysis, store the samples at 40°F.

NYLON, TEFLON EXTRACTION AND ANALYTICAL PROTOCOL

A. Nylon filter

Using tweezers, place the nylon filter into a clean sample bottle. Pipette in 20 ml of 0.003 N NaOH. Use a clean piece of Teflon tubing to submerge the filter under solution. Cap bottle and sonicate for 30 min. Analyze the solution by ion chromatography for NO_3^-. Prior to analysis, store the samples at 40°F.

B. Teflon filter

Using tweezers, place the Teflon filter into a clean sample bottle. Pipette in 20 ml of deionized water. Use a clean piece of Teflon tubing to submerge the filter under solution. Cap the bottle and sonicate for 30 min. Analyze the solution by ion chromatography for SO_4^{2-} and NO_3^-, by ion specific electrode for H^+, and colorimetric techniques for NH_4^+. Prior to analysis, store the sample at 40°F.

C. 0.003 N NaOH solution

Weigh out 0.06 grams of NaOH. Place in a 500 ml volumetric flask and dilute to 500 ml with deionized water. Cap and invert the bottle a few times to dissolve NaOH. (0.12 g of NaOH could be used with 1 liter of water.)

PREPARATION OF SAMPLE BOTTLES

A. New bottles and caps: Rinse with deionized water, then place upside-down on a clean Kimwipe to dry overnight (approx. 15 hours). Recap until use.

B. Previously used bottles: Remove any old labels. Rinse with hot tap water three times. Rinse with deionized water three times. Fill the bottles with deionized water, cap, and allow to soak overnight. The next day, empty each bottle and shake as dry as possible. Place bottles and caps upside down on a clean Kimwipe to dry overnight. Recap until use.

D. Be sure to label all sample bottles before placing denuder extracts or filters into them. Put a piece of scotch tape over the label to ensure it stays on the bottle.

TEFLON FILTER SUBMERGERS

A. Cut small sections, a nominal 2-3/8-in to 2-1/2-in long, from a clean (preferably virgin) piece of 5/16-in OD Teflon tubing,

B. At one end of the small section, make three 1/2-in longitudinal cuts. Pull the newly cut flaps out to form a base (see Figure 4).

C. Use these Teflon sections to hold the Teflon and nylon filters under solution in the 30 ml size bottles. The lid of the bottle should fit snugly down on top of the Teflon section, compressing the flaps. If the cap won't close properly, cut the flaps up higher to spread the base out further and lower the height.

D. Remove the Teflon section from the sample bottle after the analysis is complete.

E. Wash used pieces by first rinsing with deionized water, then sonicate 30 min in a beaker of deionized water. Dry on Kimwipe towels. Handle clean pieces with gloves on. Store filter submergers in a clean, sealed, plastic bag.

LEAK CHECKING

Once assembled, the ADS should be checked for leaks before mounting outdoors. Using a small vacuum pump with a pressure gauge, attach the pump inlet to the cyclone inlet by a secure piece of rubber tubing. The pump should be turned on, and a nominal vacuum of 200-300 mm Hg should be reached. Using a valve, close off the flow downstream of the gauge, before the pump, keeping pump turned on. The vacuum should fall no more than 100 mm in 20 seconds. If the vacuum falls off more quickly, re-tighten all joints.

Note: If unable to stop leaks by tightening fittings, 1-1/2-in. hose clamps may be necesary on the collars of the cyclone couplings and filter pack. Avoid overtightening clamps as it may deform the threads.

EQUIPMENT AND SUPPLIES
(for one site, with duplicate runs)

Equipment

6	Annular denuders
2	Filter packs
4	Screens for filter pack
4	O-rings for filter pack
2	Cyclones
4	Teflon denuder couplings
2	Anderson flow modules (or equivalent)
2	1/2-in i.d. sample flow line from flow module to ADS, plus fittings
2	Electrical connections from flow module to ADS
2	Sample boxes with fan and light
1	Min/max thermometer
1	Dry test meter with hoses and fittings
1	Decimal minute stopwatch
1	Tweezers - flat tipped
1	Zero air source
1	Plastic tub for washing and storage of denuders
2	10 ml pipets or 2 repipettors
1	Pipet bulb
2	100 ml volumetric flask
1	500 ml volumetric flask
1	Analytical balance, accuracy to 0.001 gram
1	Vacuum pump with vacuum gauge and valve in line
1	Rubber tube and hose clamps for vacuum pump

Supplies

2/wk	47 mm Zefluor (Teflon) filters 2 μm pore (Gelman part no. 66509)
2/wk	47 mm Nylasorb (nylon) filters 1 μm pore (Gelman part no. P5PJ047)
	Sodium carbonate ACS cert. anhydrous
	Glycerol ACS cert.
	Citric acid monohydrate powder ACS cert.
	Methanol ACS HPLC grade (or reagent grade)
	Sodium hydroxide ACS reagent grade
	Hydrogen peroxide 30 percent
	Acetone ACS cert.
	Deionized water
12/wk	30 ml thick-walled polyethylene bottles (Nalgene no. 2104)
	Disposable plastic gloves
	Kimwipes
	Gummed labels 1/2" x 2"
	Teflon tubing 5/16" x 5', for cutting into filter submergers
	Clear cellophane tape
	Plastic bags

Spare Parts

2-4 Denuders per site
Lightbulbs, size GE 1156 7LE
6 1-1/2 in. hose clamps

CALCULATIONS

A. Flow measurement

$$\frac{20\ \text{L}}{\text{measured decimal minutes (avg. of 3)}} = \text{flow Lpm uncorrected}$$

Flow x ab = Flow SLPM where

a = dry gas meter calibration correction factor
b = correction factor to STP, 760 mm Hg and 0°C

$$CF = \frac{P_1 \quad 273}{760 \quad (273+T_1)}$$

B. Total mass loading

1. µg/ml ion from I.C. x 20 ml extract = total µg

2. For HONO, HNO_3, SO_2

   use Denuder 1 minus Denuder 2

3. For NH_3

   use total µg on citric acid denuder minus blank value

4. For NH_4, SO_4^{2-}, NO_3

   use µg on Teflon filter minus blank

5. For NO_3^- volatile

   use µg on nylon filter minus blank

6. For H^+

   use pH from Teflon filter and convert to n mol units

   $10^{-pH}\ 2x10^7$ = nmol

   use n mol on Teflon filter minus blank

C. Concentrations

1.a. Total µg each species ÷ m^3 sampled = µg/m^3

b. $H^+ \div m^3$ = nmol/m^3

2. I.C. data is in ION state; must be converted to each species by multiplying correct conversion.

$$\frac{HONO}{NO_2^-} \quad \frac{47}{46} = 1.0217 \qquad \frac{HNO_3}{NO_3^-} \quad \frac{63}{62} = 1.0161 \qquad \frac{SO_2}{SO_4^{2-}} \quad \frac{64}{96} = 0.6667$$

$$\frac{NH_3}{NH_4^+} = \frac{17}{18} = 0.9444$$

For example, HONO is measured as NO_2^-. To express the mass of NO_2^- as HONO, multiply by 1.0217.

$$1.0217\ (\mu g\ NO_2^-) = \mu g\ HONO$$

3. $\frac{\mu g/m^3}{M.W.}(1000) = n\ mol/m^3$

REFERENCES

Possanzini, M., Febo, A., and Liberti, A. (1983). "New Design of High Performance Denuder for the Sampling of Atmospheric Pollutants," Atmos. Environ. 17, 2605-2610.

Stevens, R. K., Paur, R. J., Allegrini, I., DeSantis, F., Febo, A., Perrino, C., Possanzini, M., Cox, K. W., Estes, E. D., Turner, A. R., and Sickles, J. E., II. (1985). Measurement of HNO_3, SO_2, NH_3, and Particulate Nitrate with an Annular Denuder System. In Proceedings of Fifth Annual National Symposium on Recent Advances in the Measurement of Air Pollution. May 14-16, 1985. Raleigh, NC.

Sickles, J. E. II, Perrino, C., Allegrini, I., Febo, A., Possanzini, M., and Paur, R. J. Performance and Results of the Annular Denuder System in the Sampling and Analysis of Ambient Air Near Los Angeles. In Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants. EPA Report No. 600/9-86-013, pp. 522-533.

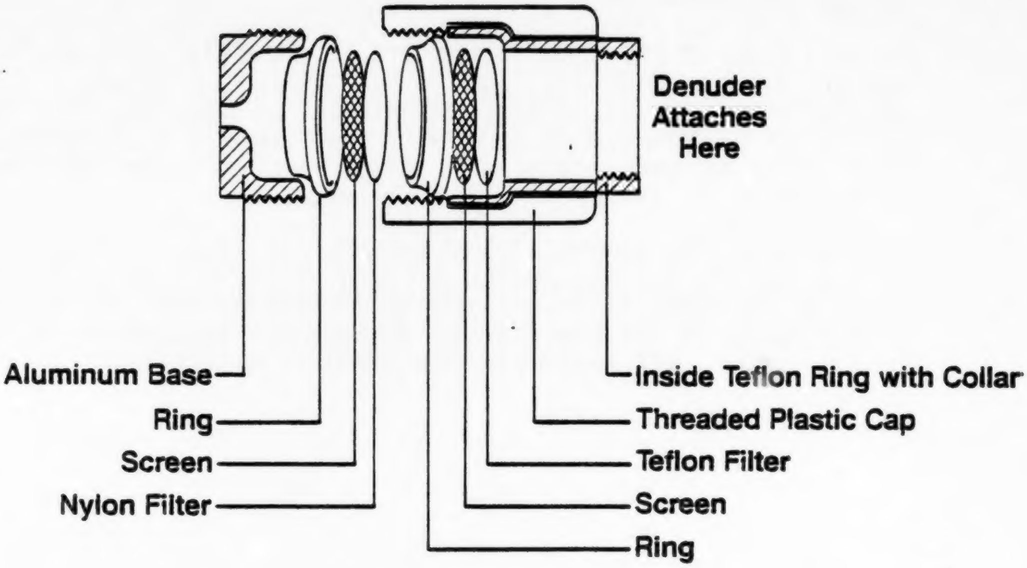
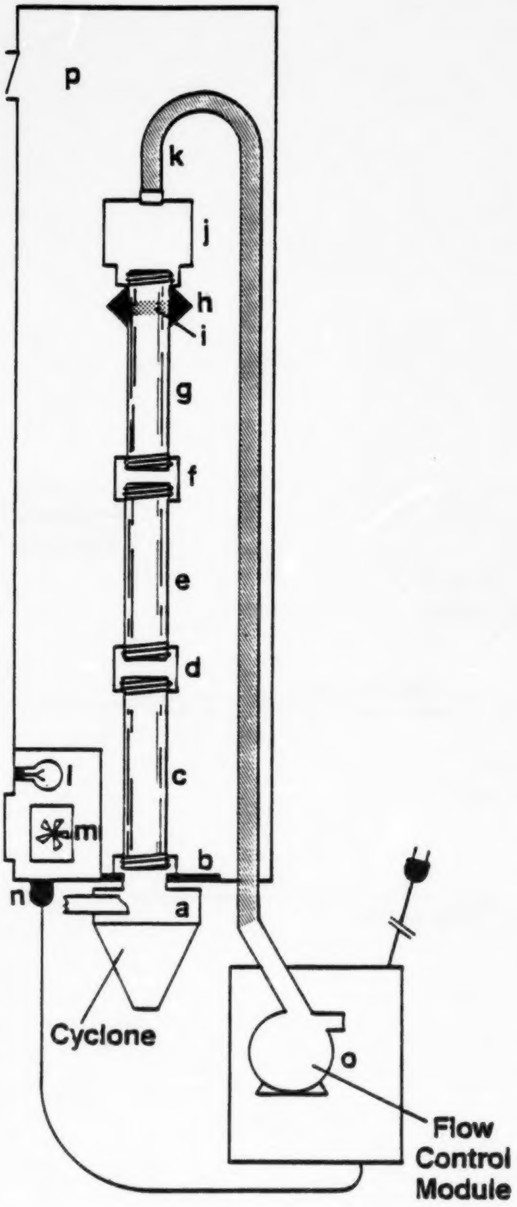

Denuder
Attaches
Here
Aluminum Base
Ring
Screen
Nylon Filter
Inside Teflon Ring with Collar
Threaded Plastic Cap
Teflon Filter
Screen
Ring

Figure C-1. Filter pack assembly.


p
k
j
h
i
g
f
e
d
c
l
m
b
n
a
Cyclone
o
Flow Control Module

a. TFE Teflon cyclone
b. Aluminum shield
c. Na_2CO_3-coated denuder
d. Teflon coupling
e. Na_2CO_3-coated denuder
f. Teflon coupling
g. Citric acid-coated denuder
h. Support bracket
i. Velcro fastener
j. Filter pack
k. Flow line
l. Light bulb
m. Fan
n. Electrical connection
o. Flow control module
p. Sampler box

Figure C-2. Assembly of ADS.

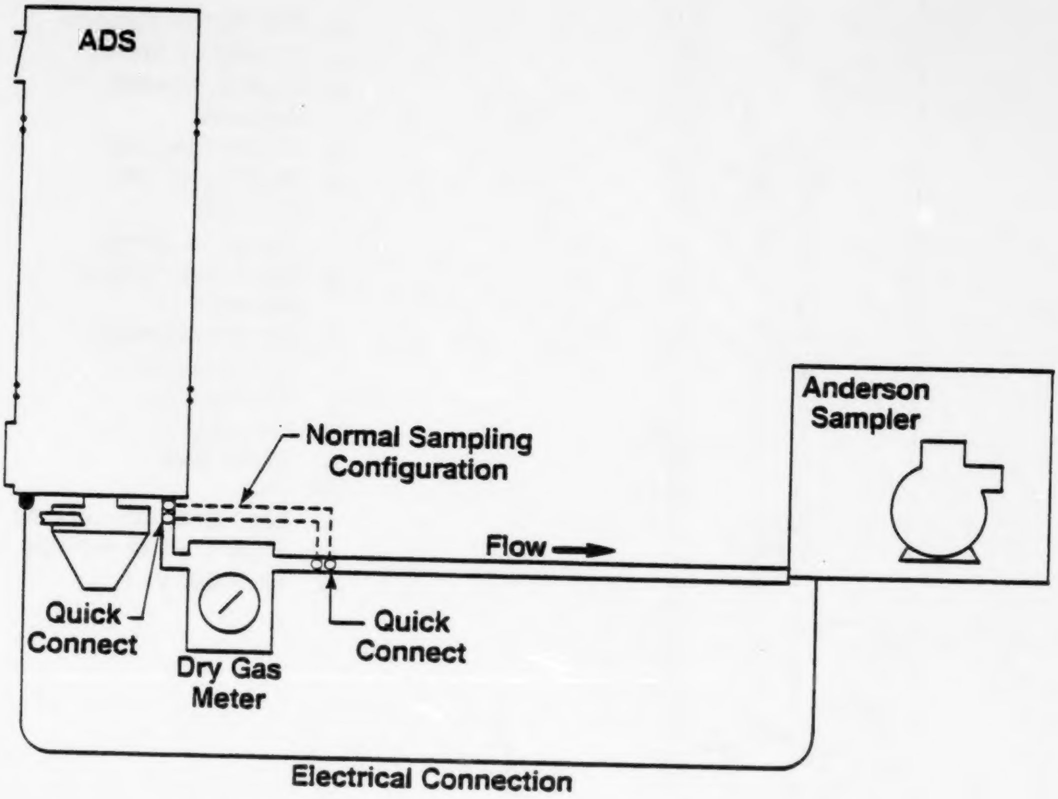

ADS
Normal Sampling Configuration
Anderson Sampler
Flow
Quick Connect
Dry Gas Meter
Quick Connect
Electrical Connection

Figure C-3. Measuring flow.

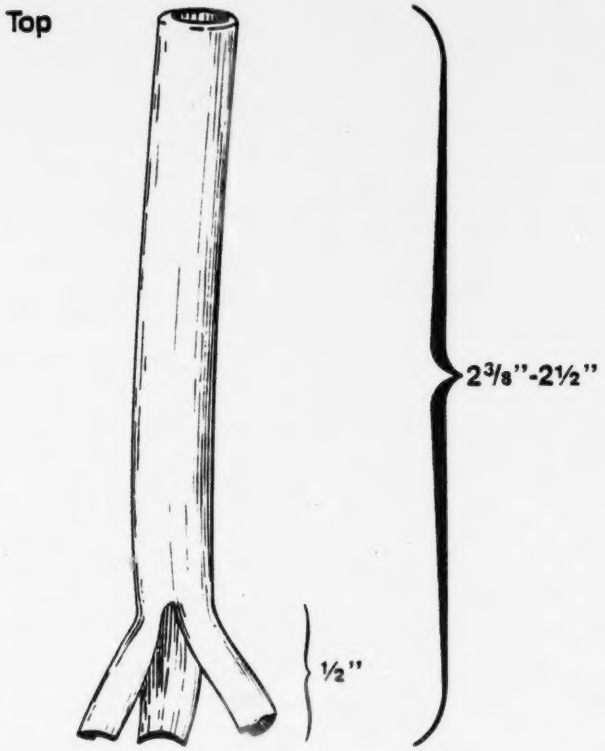


Figure C-4. Teflon filter submerger.

APPENDIX D

PAN INTERFERENCE TESTING WITH THE LMA-3 NO_2 DETECTOR

SUMMARY

The LMA-3 Luminox NO_2 Detector produced by Scintrex of Ontario, Canada was tested in the laboratory with atmospheres containing nitrogen dioxide (NO_2) and peroxyacetyl nitrate (PAN). The concentrations of the tested gases ranged from 10 ppb to 100 ppb under both dry and humid conditions. The LMA-3 showed an average NO_2 response of 99 percent and an approximate PAN response of 54 percent. In a mixture of NO_2 plus PAN, the approximate response was 92 percent of the total. This indicates that for the conditions tested, PAN may act as a significant interferent in the measurement of NO_2 using the LMA-3.

EXPERIMENTAL

The LMA-3 was maintained at 30°C in a constant temperature chamber. "High sensitivity" Luminol solution supplied by Scintrex was used.

PAN was synthesized in iso-octane (1). The concentration was determined by FT-IR. A known amount of PAN (in µl) was injected through a septum into a zero air line which was used to fill 130-liter Teflon bags. The NO_2 source was a reference gas cylinder. A known volume of NO_2 was drawn into a gas syringe and injected, using the previously described delivery system, into Teflon bags.

For each test, four Teflon bags were used. One bag contained NO_2, one bag contained PAN, one bag contained a mixture of NO_2 plus PAN, and one bag contained zero air. The concentrations of the bagged samples were verified by a chemiluminescent (CLM) Bendix 8101C NO_x analyzer and a gas chromatograph with an electron capture detector (GC-EC). The target concentrations of NO_2 and PAN were 10 ppb, 25 ppb, and 100 ppb each, under both dry and humid (60-70% RH) conditions.

Preceding page blank

RESULTS

Laboratory tests of PAN decay rates were conducted over 3-hour periods at target concentrations of 25 and 100 ppb. Tests were conducted using atmospheres containing PAN and both PAN and NO_2. The mean PAN decay coefficient for four tests was 2.9 percent per hour, in good agreement with reported values (2). This also indicates tnat the results of the current study do not require correction for PAN decay.

The LMA-3 displayed a distinct voltage sensitivity: whenever the fan or heater turned on inside the constant temperature chamber, the output voltage dropped to near zero and quickly returned to its previous position. The result is a strip chart trace with many spikes.

EPA specified that zero and span pots were not to be adjusted during the tests. Over the testing period, the LMA-3 ppb response exceeded the delivered nominal NO_2 concentration by 30 percent.

Daily calibrations of the LMA-3 were performed using NO_2 from a reference cylinder. These calibrations were verified by comparison with the CLM NO_x analyzer. Throughout the testing period, the calibration of the LMA-3 remained linear. The slope of the calibration curve, however, changed an average of 5.8 ± 19.4% from day to day.

The LMA-3 showed an average NO_2 response of 99.4% of the nominal value and 98.3% of the CLM value. When a combination of PAN plus NO_2 was tested, the LMA-3 response was 92.3% of the nominal value and 92.4% of the CLM value. With an atmosphere of PAN, the LMA-3 response was 53.8% of the nominal value and 50.4% of the CLM value. The CLM response was approximately 100% of the nominal values for NO_2, PAN, and mixtures of the two. Differences in humidity exerted no apparent influence on the response of the LMA-3.

REFERENCES

1. Holdren, M. W. and Spicer, C. W. (1984). Field Compatible Calibration Procedure for Peroxyacetyl Nitrate. Environ. Sci. Technol. 18: 113-116.

2. Grosjean, D. (1985). Wall Loss of Gaseous Pollutants in Outdoor Teflon Chambers. Environ. Sci. Technol. 16: 655-660.

APPENDIX E

COMPARISON OF THE ABSORPTION OF HNO_3 BY TWO BRANDS OF NYLON FILTERS

A study was conducted to compare the absorption of nitric acid by two different brands of nylon filters. Gelman Nylasorb 1 μm filters were compared with Schleicher & Schuell (S&S) nylon 1.2 μm filters.

The HNO_3 was generated from a permeation tube, and all tests were conducted at 50 percent RH and 25°C. Filter extraction was performed by sonicating each filter for 30 minutes in 10 ml of 0.003 N NaOH. Nitrate analysis of the extract solutions was by ion chromatography (IC).

The S&S filters had higher blank values for NO_3^- and SO_4^{2-} (2.37 μg and 17.3 μg) than the Gelman filters (< 0.5 μg NO_3^- and 2.94 μg SO_4^{2-}). Both brands of filters had negligible blank nitrite values.

Filters of each type were spiked with a KNO_3 solution. The average recovery efficiency for S&S filters was 100 percent, while average recovery efficiency for Gelman filters was 99 percent.

The average blank-corrected recovery for three HNO_3 loading experiments with S&S filters is 26.2 μg/filter, while the average recovery for three Gelman filters is 23.3 μg/filter. The ratio of mean recoveries is 1.13, indicating that more nitrate is recovered from the S&S than the Gelman nylon filters in this study. A statistical comparison of the mean recoveries from the two filter types does not show a significant difference at the 0.1 level.

APPENDIX F

DATA SUMMARY FOR FALL 1986 FIELD STUDY USING ADS AND TFR

Preceding page blank

ADS Concentration (ug/m3) Data for Daily Intensive Field Study

			*** Gaseous & *** ** Particulate **		Particulate							
Day No.	Sampler No.	Date Start-End	Total NO_3	Total NH_3+NH_4	Total NH_4	Total SO_4	Fine NH_4	Fine SO_4	Fine NO_3	Teflon NO_3	Nylon NO_3	Teflon H^+
	ADS1	HNO_3 SPIKE1	46.083	8.000	5.188	16.578	3.010	15.212	0.257	-0.211	0.468	149.858
	ADS3	HNO_3 SPIKE2	80.102	-4.287	-1.790	1.753	-1.084	1.564	1.060	1.336	-0.276	69.522
	ADS4	HNO_3 SPIKE2	85.612	-2.392	0.563	1.791	1.266	1.369	3.001	3.275	-0.274	195.021
1	ADS5	09/29 09/30/86	3.716	1.986	1.461	6.316	1.493	5.776	0.736	0.272	0.464	26.100
	ADS6	09/29 09/30/86	3.617	2.044	1.477	6.463	1.511	5.888	0.589	0.268	0.321	26.968
2	ADS3	09/30 10/01/86	2.658	4.200	3.375	11.657	3.231	11.326	0.544	0.129	0.415	55.564
	ADS4	09/30 10/01/86	2.846	3.686	3.024	10.825	2.948	10.564	0.604	0.290	0.314	45.606
3	ADS5	10/01 10/02/86	3.565	4.704	4.044	13.714	3.922	13.401	0.354	0.073	0.281	56.921
	ADS6	10/01 10/02/86	3.782	4.404	3.895	14.185	3.807	13.886	0.390	0.091	0.299	61.796
4	ADS3	10/02 10/03/86	2.479	2.446	1.652	5.645	1.652	5.411	0.166	0.040	0.126	23.253
	ADS4	10/02 10/03/86	2.018	2.247	1.339	6.140	1.370	5.948	0.061	0.073	-0.012	20.026
5	ADS5	10/03 10/04/86	3.226	3.711	2.550	8.743	2.584	8.559	0.213	0.047	0.166	42.267
	ADS6	10/03 10/04/86	3.556	3.512	2.853	8.448	2.888	8.291	0.291	0.106	0.185	36.081
6	ADS3	10/04 10/05/86	3.301	3.622	2.768	9.077	2.745	8.761	0.499	0.282	0.218	48.310
	ADS4	10/04 10/05/86	3.148	3.533	2.636	8.935	2.624	8.706	0.345	0.121	0.224	35.952
7	ADS5	10/05 10/06/86	3.092	2.079	1.509	5.853	1.413	5.619	0.458	0.352	0.106	42.487
	ADS6	10/05 10/06/86	2.923	2.179	1.571	5.766	1.466	5.482	0.190	0.090	0.100	33.457
8	ADS3	10/06 10/07/86	2.245	1.485	0.642	2.746	0.673	2.551	0.186	0.088	0.098	22.191
	ADS4	10/06 10/07/86	2.046	1.497	0.810	2.980	0.665	2.734	0.113	0.016	0.097	22.331
9	ADS5	10/07 10/08/86	3.926	1.669	1.115	4.204	1.082	3.535	0.265	0.145	0.120	11.290
	ADS6	10/07 10/08/86	3.814	1.622	1.141	4.056	1.098	3.615	0.363	0.176	0.187	11.081
10	ADS4	10/08 10/09/86	3.121	1.792	0.798	4.263	0.831	3.560	0.646	0.459	0.187	30.651
	ADS3	10/08 10/09/86	3.121	1.847	0.907	4.425	0.809	3.817	0.807	0.542	0.265	10.628
11	ADS5	10/09 10/10/86	3.671	3.424	2.361	7.357	2.394	6.992	2.462	0.361	2.101	22.796
	ADS6	10/09 10/10/86	3.387	3.548	2.176	7.392	2.208	7.004	2.109	0.380	1.729	26.046
12	ADS4	10/10 10/11/86	3.143	1.620	1.302	4.914	1.227	4.278	0.750	0.387	0.363	18.369
	ADS3	10/10 10/11/86	3.427	1.810	1.382	5.230	1.413	4.634	0.893	0.427	0.465	27.243
13	ADS5	10/11 10/12/86	2.252	0.711	0.333	2.277	0.287	1.388	0.853	0.787	0.066	9.858
	ADS6	10/11 10/12/86	2.158	0.780	0.385	2.259	0.311	1.433	0.766	0.779	-0.012	2.478

ADS Concentration (ug/m3) Data for Daily Intensive Field Study

Day	Sampler	Date	************* Gaseous			*************	******** Cyclone		********
No.	No.	Start-End	HNO3	HONO	SO2	NH3	NO3	SO4	NH4
	ADS1	HNO3 SPIKE1	38.396	1.257	10.158	2.812	4.444	1.366	2.178
	ADS3	HNO3 SPIKE2	68.669	0.000	4.264	-2.497	11.092	0.188	-0.707
	ADS4	HNO3 SPIKE2	70.832	0.000	0.516	-2.954	8.836	0.422	-0.703
1	ADS5	09/29 09/30/86	1.351	1.139	3.216	0.525	1.413	0.540	-0.032
	ADS6	09/29 09/30/86	1.445	0.935	3.275	0.567	1.377	0.574	-0.034
2	ADS3	09/30 10/01/86	1.264	0.599	3.131	0.825	0.580	0.330	0.144
	ADS4	09/30 10/01/86	1.413	0.660	3.210	0.661	0.544	0.260	0.076
3	ADS5	10/01 10/02/86	2.263	0.890	8.192	0.659	0.545	0.313	0.122
	ADS6	10/01 10/02/86	2.535	0.796	8.789	0.510	0.472	0.299	0.088
4	ADS3	10/02 10/03/86	1.774	1.231	6.274	0.795	0.293	0.235	0.000
	ADS4	10/02 10/03/86	1.581	1.790	5.822	0.908	0.304	0.192	-0.032
5	ADS5	10/03 10/04/86	2.245	0.770	9.237	1.161	0.455	0.185	-0.033
	ADS6	10/03 10/04/86	2.503	0.793	9.308	0.658	0.566	0.156	-0.035
6	ADS3	10/04 10/05/86	1.839	0.445	9.145	0.854	0.666	0.316	0.023
	ADS4	10/04 10/05/86	1.833	0.476	8.971	0.898	0.615	0.229	0.012
7	ADS5	10/05 10/06/86	2.204	0.566	20.948	0.570	0.215	0.234	0.096
	ADS6	10/05 10/06/86	1.985	0.501	20.741	0.608	0.328	0.284	0.104
8	ADS3	10/06 10/07/86	1.618	0.524	12.266	0.843	0.318	0.195	-0.032
	ADS4	10/06 10/07/86	1.462	0.554	12.868	0.687	0.251	0.246	0.145
9	ADS5	10/07 10/08/86	1.960	1.306	15.493	0.554	1.466	0.670	0.032
	ADS6	10/07 10/08/86	1.756	1.280	15.023	0.481	1.284	0.441	0.043
10	ADS4	10/08 10/09/86	1.039	1.349	3.948	0.994	1.313	0.703	-0.033
	ADS3	10/08 10/09/86	0.927	1.328	4.024	0.940	1.185	0.608	0.098
11	ADS5	10/09 10/10/86	0.671	1.930	3.519	1.063	0.572	0.364	-0.033
	ADS6	10/09 10/10/86	0.729	1.835	3.615	1.372	0.583	0.389	-0.033
12	ADS4	10/10 10/11/86	1.118	0.590	11.164	0.318	1.165	0.636	0.076
	ADS3	10/10 10/11/86	1.119	0.628	11.851	0.429	1.287	0.596	-0.031
13	ADS5	10/11 10/12/86	0.379	0.363	3.366	0.378	1.054	0.889	0.045
	ADS6	10/11 10/12/86	0.227	0.400	3.346	0.395	1.118	0.827	0.074

TFR Concentration (ug/m3) Data for Daily Intensive Field Study

			** Gaseous & ** * Particulate *		************************ Particulate ************************						
Day No.	Sampler No.	Date Start-End	Total NO3	Total NH3+NH4+	Total NH4+	Total SO4	Fine NH4	Fine SO4	Fine NO3	Teflon NO3	Teflon H+
	TFR	HNO3 SPIKE1	24.799	4.067	4.518	11.766	4.605	11.406	-4.069	-0.126	74.273
	TFR	HNO3 SPIKE1	24.635	3.791	4.746	11.701	4.834	11.341	-21.368	-0.123	81.886
	TFR 2	HNO3 SPIKE2	32.512	-0.853	-2.923	1.607	-2.768	1.094	-10.625	1.801	64.779
	TFR 4	HNO3 SPIKE2	26.038	-0.139	-4.563	1.028	-4.563	1.028	-9.326	2.159	77.421
1	TFR 1	09/29 09/30/86	4.179	3.086	2.383	6.302	2.235	5.404	-0.275	0.082	23.619
	TFR 3	09/29 09/30/86	4.227	2.473	1.695	6.369	1.547	5.471	-1.601	0.085	32.739
2	TFR 2	09/30 10/01/86	2.844	3.830	3.069	10.852	2.930	10.253	-0.730	0.301	48.429
	TFR 4	09/30 10/01/86	2.783	3.957	3.640	10.901	3.502	10.306	-0.368	0.305	37.646
3	TFR 3	10/01 10/02/86	3.607	4.711	4.072	12.891	3.994	12.486	-0.814	0.242	67.233
	TFR 1	10/01 10/02/86	3.534	4.414	3.876	14.124	3.798	13.721	-0.679	0.161	56.845
4	TFR 2	10/02 10/03/86	2.319	1.941	1.383	5.461	1.333	5.207	-1.250	0.065	16.151
	TFR 4	10/02 10/03/86	2.241	2.645	2.184	5.597	2.134	5.343	-0.337	0.033	14.442
5	TFR 3	10/03 10/04/86	3.742	4.755	4.498	8.964	4.398	8.529	-1.203	0.166	39.682
	TFR 1	10/03 10/04/86	3.728	4.664	3.335	9.022	3.235	8.586	-0.225	0.158	40.646
6	TFR 2	10/04 10/05/86	3.125	4.536	3.475	8.625	3.425	8.078	-1.809	0.124	27.080
	TFR 4	10/04 10/05/86	3.143	4.494	3.548	8.839	3.498	8.292	-0.789	0.110	16.726
7	TFR 3	10/05 10/06/86	2.695	2.497	1.906	5.470	1.860	5.177	-1.652	-0.020	9.828
	TFR 1	10/05 10/06/86	2.698	2.559	1.928	6.157	1.882	5.864	-0.446	0.060	24.083
8	TFR 2	10/06 10/07/86	1.975	1.721	1.038	2.770	0.987	2.578	-0.802	-0.020	9.524
	TFR 4	10/06 10/07/86	2.042	1.516	0.919	2.665	0.868	2.473	-0.289	0.069	6.876
9	TFR 1	10/07 10/08/86	3.798	2.127	1.796	4.133	1.700	3.664	-1.479	0.184	15.630
	TFR 3	10/07 10/08/86	3.933	2.180	1.724	4.548	1.628	4.079	-1.560	0.207	1007049
10	TFR 4	10/08 10/09/86	3.370	2.416	1.891	4.159	1.849	3.439	-1.606	0.153	4.977
	TFR 2	10/08 10/09/86	3.343	1.738	1.336	4.327	1.294	3.606	-0.897	0.196	16.880
11	TFR 3	10/09 10/10/86	3.757	3.421	2.728	6.585	2.445	5.850	1.517	1.924	16.400
	TFR 1	10/09 10/10/86	3.747	3.496	2.446	6.598	2.163	5.863	1.070	1.863	20.420
12	TFR 4	10/10 10/11/86	3.466	2.007	1.446	4.957	1.309	4.134	-0.919	0.239	6.500
	TFR 2	10/10 10/11/86	3.537	2.158	1.549	5.077	1.413	4.254	-0.992	0.214	11.093
13	TFR 1	10/11 10/12/86	1.895	1.269	0.913	2.156	0.773	1.286	-0.295	0.092	1.818
	TFR 3	10/11 10/12/86	1.955	1.065	0.463	2.190	0.323	1.320	-0.512	0.149	5.139

TFR Concentration (ug/m3) Data for Daily Intensive Field Study

Day	Sampler	Date	************** Gaseous **************				********* Cyclone ********			QC Ratio
No.	No.	Start-End	HNO3	NO2	SO2	NH3	NO3	SO4	NH4	HNO3
	TFR	HNO3 SPIKE1	26.705	15.621	5.515	-0.451	1.514	0.360	-0.088	0.100
	TFR	HNO3 SPIKE1	43.836	13.384	10.105	-0.955	1.514	0.360	-0.088	0.166
	TFR 2	HNO3 SPIKE2	39.830	9.350	1.455	2.071	4.031	0.514	-0.156	0.116
	TFR 4	HNO3 SPIKE2	36.707	1.850	-13.500	4.423	4.031	0.514	-0.156	0.114
1	TFR 1	09/29 09/30/86	2.077	20.378	2.149	0.702	2.315	0.898	0.148	0.098
	TFR 3	09/29 09/30/86	3.453	21.516	2.700	0.779	2.315	0.898	0.148	0.158
2	TFR 2	09/30 10/01/86	2.775	13.332	3.350	0.761	0.792	0.596	0.138	0.115
	TFR 4	09/30 10/01/86	2.356	13.429	1.949	0.317	0.792	0.596	0.138	0.101
3	TFR 3	10/01 10/02/86	3.710	16.877	7.235	0.639	0.662	0.400	0.077	0.109
	TFR 1	10/01 10/02/86	3.504	17.365	6.549	0.538	0.662	0.400	0.077	0.105
4	TFR 2	10/02 10/03/86	3.179	24.507	5.546	0.558	0.382	0.254	0.050	0.140
	TFR 4	10/02 10/03/86	2.186	24.948	5.250	0.460	0.382	0.254	0.050	0.101
5	TFR 3	10/03 10/04/86	3.904	13.207	7.084	0.257	1.018	0.435	0.100	0.123
	TFR 1	10/03 10/04/86	2.912	13.593	7.541	1.328	1.018	0.435	0.100	0.092
6	TFR 2	10/04 10/05/86	3.875	10.354	6.810	1.060	1.030	0.547	0.051	0.159
	TFR 4	10/04 10/05/86	2.873	10.842	7.311	0.945	1.030	0.547	0.051	0.117
7	TFR 3	10/05 10/06/86	3.829	20.646	21.240	0.591	0.437	0.293	0.046	0.150
	TFR 1	10/05 10/06/86	2.625	20.923	20.744	0.632	0.437	0.293	0.046	0.102
8	TFR 2	10/06 10/07/86	2.440	19.118	10.313	0.683	0.293	0.192	0.051	0.127
	TFR 4	10/06 10/07/86	1.996	14.467	6.816	0.597	0.293	0.192	0.051	0.099
9	TFR 1	10/07 10/08/86	3.687	29.001	13.605	0.331	1.559	0.469	0.096	0.142
	TFR 3	10/07 10/08/86	3.907	34.574	16.322	0.456	1.559	0.469	0.096	0.141
10	TFR 4	10/08 10/09/86	3.045	24.339	3.208	0.525	1.834	0.720	0.042	0.180
	TFR 2	10/08 10/09/86	2.309	25.156	2.495	0.402	1.834	0.720	0.042	0.139
11	TFR 3	10/09 10/10/86	1.190	28.667	1.466	0.693	0.937	0.735	0.283	0.037
	TFR 1	10/09 10/10/86	1.626	29.994	1.857	1.051	0.937	0.735	0.283	0.051
12	TFR 4	10/10 10/11/86	2.647	16.040	10.762	0.561	1.718	0.823	0.137	0.130
	TFR 2	10/10 10/11/86	2.793	15.214	10.565	0.608	1.718	0.823	0.137	0.132
13	TFR 1	10/11 10/12/86	0.709	9.557	2.478	0.356	1.365	0.870	0.140	0.145
	TFR 3	10/11 10/12/86	0.988	10.424	1.766	0.602	1.365	0.870	0.140	0.176

ADS Concentration (ug/m3) Data for Weekly Study

				*** Gaseous & *** ** Particulate **		****************************** Particulate ******************************							
Week No.	Sampler No.	Date Start-End		Total NO3	Total NH3+NH4	Total NH4	Total SO4	Fine NH4	Fine SO4	Fine NO3	Teflon NO3	Nylon NO3	Teflon H+
1	ADS1	08/26	09/02/86	NA (1)	NA (1)	NA (1)	NA (1)	0.139	4.738	0.359	0.050	0.310	19.646
2	ADS1	09/02	09/09/86	NA (1)	NA (1)	NA (1)	NA (1)	1.060	6.266	0.474	0.003	0.471	34.141
	ADS2	09/02	09/09/86	NA (1)	NA (1)	NA (1)	NA (1)	1.106	6.050	0.484	0.069	0.415	32.561
3	ADS1	09/09	09/16/86	NA (1)	NA (1)	NA (1)	NA (1)	1.171	7.839	0.556	-0.000	0.557	32.652
	ADS2	09/09	09/16/86	NA (1)	NA (1)	NA (1)	NA (1)	1.670	7.874	0.547	-0.000	0.547	30.689
4	ADS1	09/16	09/23/86	4.285	2.097	1.754	10.289	1.618	9.880	0.552	0.017	0.534	33.066
	ADS2	09/16	09/23/86	4.280	2.015	1.476	10.889	1.352	10.365	0.554	-0.003	0.557	39.895
5	ADS1	09/23	09/30/86	4.375	4.929	4.814	13.731	4.746	13.406	0.618	0.022	0.596	27.954
	ADS2	09/23	09/30/86	4.374	5.318	4.629	13.576	4.538	13.265	0.580	0.037	0.543	30.829
6	ADS1	09/30	10/07/86	3.987	2.800	1.974	8.391	1.979	8.185	0.388	0.023	0.365	31.337
	ADS2	09/30	10/07/86	4.083	2.686	1.910	8.232	1.840	7.951	0.390	0.030	0.360	27.377
7	ADS1	10/07	10/12/86	3.560	2.166	1.477	4.811	1.388	4.286	0.956	0.087	0.869	9.044
	ADS2	10/07	10/12/86	3.886	2.196	1.437	5.126	1.355	4.576	1.134	0.130	1.004	9.603
8	ADS1	10/14	10/21/86	3.645	2.147	1.765	5.968	1.722	5.780	0.593	0.047	0.547	10.013
	ADS2	10/14	10/21/86	3.740	1.977	1.592	5.633	1.545	5.458	0.558	0.045	0.513	9.913
9	ADS	10/21	10/28/86	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)
10	ADS5	10/28	11/04/86	3.749	1.606	1.263	6.448	1.267	6.064	0.753	0.062	0.690	11.355
	ADS6	10/28	11/04/86	3.884	1.894	1.485	6.392	1.474	5.947	0.699	0.054	0.644	12.511
11	ADS3	11/04	11/11/86	4.742	2.103	1.843	8.864	1.767	8.226	0.745	0.061	0.684	13.811
	ADS4	11/04	11/11/86	4.280	2.096	1.696	8.359	1.651	7.734	0.696	0.055	0.641	15.114
12	ADS5	11/11	11/18/86	3.835	1.647	1.556	6.651	1.404	5.740	1.069	0.082	0.987	24.247
	ADS6	11/11	11/18/86	4.217	1.730	1.581	7.196	1.577	6.304	1.246	0.090	1.156	24.782
13	ADS3	11/18	11/25/86	3.307	1.381	1.286	6.480	1.232	6.105	0.683	0.028	0.655	22.500
	ADS4	11/18	11/25/86	3.746	1.355	1.361	6.638	1.312	6.212	0.812	0.053	0.759	27.396
14	ADS5	11/25	12/02/86	3.521	1.215	0.961	4.458	0.919	4.176	1.056	0.190	0.867	9.740
	ADS6	11/25	12/02/86	3.416	1.034	0.827	3.952	0.798	3.654	1.033	0.173	0.860	9.714

1) Data not available - Cyclone not extracted.
2) Data not available - Sampler filters clogged due to nearby agricultural burning.

ADS Concentration (ug/m3) Data for Weekly Study

Week	Sampler	Date		Gaseous				Cyclone		
No.	No.	Start-End		HNO3	HONO	SO2	NH3	NO3	SO4	NH4
1	ADS1	08/26	09/02/86	1.338	0.052	5.789	0.305	NA (1)	NA (1)	NA (1)
2	ADS1	09/02	09/09/86	1.194	0.340	5.928	0.432	NA (1)	NA (1)	NA (1)
	ADS2	09/02	09/09/86	1.333	0.533	6.230	0.495	NA (1)	NA (1)	NA (1)
3	ADS1	09/09	09/16/86	1.371	0.156	6.974	0.422	NA (1)	NA (1)	NA (1)
	ADS2	09/09	09/16/86	1.459	0.127	6.660	0.420	NA (1)	NA (1)	NA (1)
4	ADS1	09/16	09/23/86	1.945	0.443	7.682	0.343	0.765	0.409	0.135
	ADS2	09/16	09/23/86	2.048	0.457	7.827	0.540	0.868	0.524	0.123
5	ADS1	09/23	09/30/86	2.091	0.235	6.928	0.115	0.615	0.325	0.067
	ADS2	09/23	09/30/86	1.995	0.291	6.650	0.688	0.661	0.311	0.091
6	ADS1	09/30	10/07/86	2.114	0.037	9.566	0.826	0.399	0.206	-0.004
	ADS2	09/30	10/07/86	2.296	0.010	9.540	0.776	0.427	0.280	0.070
7	ADS1	10/07	10/12/86	1.074	0.749	8.276	0.689	1.150	0.524	0.089
	ADS2	10/07	10/12/86	1.124	0.792	8.917	0.759	1.211	0.550	0.082
8	ADS1	10/14	10/21/86	1.782	0.056	10.472	0.383	0.355	0.189	0.043
	ADS2	10/14	10/21/86	1.602	NA	12.962	0.385	0.412	0.175	0.047
9	ADS	10/21	10/28/86	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)	NA (2)
10	ADS5	10/28	11/04/86	1.255	0.290	11.439	0.343	0.785	0.384	-0.004
	ADS6	10/28	11/04/86	1.338	0.553	12.055	0.409	0.983	0.446	0.011
11	ADS3	11/04	11/11/86	2.119	0.176	11.550	0.259	0.708	0.638	0.076
	ADS4	11/04	11/11/86	1.950	0.311	10.598	0.400	0.654	0.625	0.045
12	ADS5	11/11	11/18/86	1.125	NA	14.847	0.091	1.051	0.911	0.153
	ADS6	11/11	11/18/86	1.498	0.983	19.138	0.149	1.042	0.892	0.004
13	ADS3	11/18	11/25/86	1.505	0.321	12.702	0.095	0.509	0.375	0.054
	ADS4	11/18	11/25/86	1.609	0.121	14.694	-0.006	0.558	0.427	0.049
14	ADS5	11/25	12/02/86	1.431	0.885	11.415	0.254	0.640	0.282	0.042
	ADS6	11/25	12/02/86	1.197	0.730	13.411	0.208	0.665	0.298	0.029

1) Data not available - Cyclone not extracted.
2) Data not available - Sampler filters clogged due to nearby agricultural burning.

APPENDIX G

EMSL FALL 1986 DRY DEPOSITION METHODS COMPARISON STUDY -- ACROSS-METHODS COMPARISON

by

J. E. Sickles, II, Research Triangle Institute
Research Triangle Park, North Carolina 27709

W. A. McClenny and R. J. Paur
Monitoring Methods Section, Methods Development Branch
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Contract No. 68-02-4079

and EPA In-House

Project Officers

W. A. McClenny and R. J. Paur
Methods Development and Analysis Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

Preceding page blank

DISCLAIMER

Although the information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. EPA 68-02-4079 to Research Triangle Institute, Research Triangle Park, NC, under Contract No. EPA 68-02-4444 to Northrop Services, Environmental Systems, and under Contract No. EPA 68-02-4152 to Unisearch Associates, Toronto, Ontario, Canada, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, has responsibility for assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency, including the EPA component of the National Acid Precipitation Assessment Program (NAPAP).

Recently, a methods development project devoted to testing existing and newly developed dry deposition monitors was completed. Work during the past 3 years included evaluation of existing procedures adapted for dry deposition monitoring, development of new techniques, and testing of the most promising candidate methods under actual field conditions. This latter task required a major field test that involved operation of a Transition Flow Reactor (TFR), Annular Denuder System (ADS), Canadian filter pack (FP), luminol-based NO_2 continuous monitor (LMA-3), passive sampling device for NO_2 (PSD), and a Tunable Diode Laser Absorption Spectrometer (TDLAS).

John C. Puzak
Acting Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27711

ABSTRACT

A field study was conducted to compare methods for sampling and analysis of atmospheric constituents that are important contributors to acidic dry deposition. Three multicomponent samplers were used: the Canadian filter pack (FP), the annular denuder system (ADS), and the transition flow reactor (TFR). A tunable diode laser absorption spectrometer (TDLAS) provided continuous reference measurements of NO_2 and HNO_3. Nitrogen dioxide was also monitored with continuous luminol-based chemiluminescence monitors (i.e., Scintrex Model LMA-3) and with passive sampling devices (PSDs). The study was designed to provide a data base for statistical comparison of the various methods with emphasis on the multicomponent samplers under consideration for use in a national dry deposition network. The TDLAS was not available for a sufficient period of time to permit the collection of enough weekly samples to simulate network operation adequately on a statistical basis. As a result, daily sampling periods were planned.

The study was conducted at the EPA dry deposition station in Research Triangle Park, NC between 29 September and 12 October, 1986. Daily averaging and/or sampling times were employed for the 13-day study; weekly samples were also collected, but results from these samples are not compared in this report. Ambient concentrations of the following constituents are compared: total particulate and gaseous nitrate, nitric acid, nitrogen dioxide, total particulate sulfate, and total particulate ammonium.

CONTENTS

Page

Foreword 183
Abstract 184
Figures 186
Tables 187
Acknowledgement 189

1. Introduction 191
2. Summary and Conclusions 193
3. Experimental 195
4. Results and Discussion 203

References 215

FIGURES

Number — Page

G-1 Location of sampling stations for the study 197

G-2 Annular denuder system, transition flow reactor, and personal sampling device placement on dry deposition station 198

G-3 Filter pack and transition flow reactor (second daily sampler) placement on dry deposition station 199

G-4 Mean daily Total NO_3^- concentrations from ADS, TFR, and FP samples 205

G-5 Mean daily HNO_3 concentrations from ADS, TFR, TFR (FP), FP, and TDLAS techniques 206

G-6 Mean daily HNO_3 concentrations from TFR, TFR (FP), TFR (EPA) and consensus of ADS, FP, and TDLAS 207

G-7 Mean daily NO_2 concentrations from TFR and TDLAS techniques 208

G-8 Mean daily NO_2 concentrations from TDLAS, LMA-3 (1), LMA-3 (2), PSD(i), PSD(o), and TFR techniques 209

G-9 Mean daily Total (particulate) NH_4^+ concentrations from the ADS, TFR, and FP samplers and Total (NH_3 + NH_4^+) concentrations from ADS and TFR 210

G-10 Mean daily Total (particulate) SO_4^{2-} concentrations from ADS, TFR, and FP samplers 211

TABLES

Number		Page
G-1	Session under dry deposition methods comparison study at the 1987 EPA/APCA symposium on measurement of toxic and related air pollutants, Research Triangle Park, North Carolina, 3-6 May 1987	192
G-2	Sampling schedule	196
G-3	Results to be compared	201
G-4	Comparison of results	204

ACKNOWLEDGEMENT

The authors acknowledge the cooperation of the individual participants as listed in Table G-1 in the careful preparation and timely submission of their data. Also, a note of thanks to G. Gallant and B. F. Magram for preparation of this manuscript.

Preceding page blank

SECTION 1
INTRODUCTION

The Environmental Monitoring Systems Laboratory (EMSL), U.S. Environmental Protection Agency (EPA), has the mandate to establish and operate a national dry deposition trends monitoring network, including the responsibility to identify and/or develop the required sampling and analysis methods. The methods evaluation and development program is being pursued primarily through a major contract to the Research Triangle Institute (RTI), Research Triangle Park, NC. Chief among the candidate sampling units are: the filter pack (FP) system, usually referred to as the Canadian filter pack because of its extensive use in Canada (1); the transition flow reactor (TFR) as reported in the open literature (2,3); and the annular denuder system (ADS) as refined from the earlier Italian version (4) to meet dry deposition monitoring needs (5).

EMSL personnel planned and organized a field evaluation of these three systems along with three other methods to compare the performance of the techniques when monitoring east coast ambient air at the dry deposition station located at the EPA facility in the Research Triangle Park, NC.

This report supplements the reporting requirements that exist for individual study participants. These participants include, in addition to RTI and EPA: Northrop Services, Environmental Sciences, a company that is currently EPA's in-house contractor; Atmospheric Environment Service (AES) of Environment Canada, the Canadian counterpart of EPA; and Unisearch Associates of Canada. Reports of the individual experimental procedures and results are expected to appear in the Proceedings of the 1987 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants to be held at the Research Triangle Park, NC, 3-6 May. Table G-1 identifies the papers for the symposium session devoted to this topic, the participants, and their affiliations.

TABLE G-1. SESSION UNDER DRY DEPOSITION - METHODS COMPARISON STUDY AT THE 1987 EPA/APCA SYMPOSIUM ON MEASUREMENT OF TOXIC AND RELATED AIR POLLUTANTS, RESEARCH TRIANGLE PARK, NC, 3-6 MAY.

Title: The EMSL Summary 1986 Dry Deposition Methods Comparison

Paper 1 -	Overview of the EMSL Methods Comparison Study W. A. McClenny, Environmental Monitoring Systems Laboratory, U.S. EPA, Research Triangle Park, NC 27711
Paper 2 -	Reference Measurements of HNO_3 and NO_2 by Diode Laser Spectroscopy G. I. Mackay and H. I. Schiff, Unisearch Associates, Inc., Toronto, Canada
Paper 3 -	Canadian Filter-Pack Measurements K. G. Anlauf, H. A. Wiebe, and D. C. MacTavish, AES, Downsview, Ontario, Canada
Paper 4 -	Measurements of HNO_3 and Other Dry Deposition Components Using the Annular Denuder System and the Transition Flow Reactor J.E. Sickles, II, L. L. Hodson, E. E. Rickman, Jr., M. L. Saeger, D. L. Hardison, A. R. Turner, C. K. Sokol, and E. D. Estes, Research Triangle Institute, Research Triangle Park, NC; R. J. Paur and T. G. Ellestad, U.S. EPA, Research Triangle Park, NC
Paper 5 -	Passive Sampling Device Measurement of NO_2 in Ambient Air J. D. Mulik, Environmental Monitoring Systems Laboratory, U.S. EPA, Research Triangle Park, NC; D. E. Williams, Northrop Services, Inc., Environmental Sciences, Research Triangle Park, NC
Paper 6 -	Luminox Measurements of Ambient NO_2 D. K. Bubacz, E. H. Daughtrey, J. D. Pleil, and K. G. Krommiller, Northrop Services, Inc., Environmental Sciences, Research Triangle Park, NC
Paper 7 -	Comparison Across Different Methods and Interpretation of Results R. J. Paur and W. A. McClenny, Environmental Monitoring Systems Laboratory, U.S. EPA, Research Triangle Park, NC

The objective of this report is to provide a timely overview and assessment of the study results so that the across-method comparisons that are available from the study can be included as part of the RTI final report. This is a preliminary report and will be followed by a more substantial report to be prepared by EPA that will include complete listings of individual data, additional results, and discussion.

SECTION 2

SUMMARY AND CONCLUSIONS

A field study was conducted to compare methods for sampling and analysis of atmospheric constituents that are important contributors to acidic dry deposition. Three multicomponent samplers were used: the Canadian filter pack (FP), the annular denuder system (ADS), and the transition flow reactor (TFR). A tunable diode laser absorption spectrometer (TDLAS) provided continuous reference measurements of NO_2 and HNO_3. Nitrogen dioxide was also monitored with continuous luminol-based chemiluminescence monitors (i.e., Scintrex Model LMA-3) and with passive sampling devices (PSDs). The study was designed to provide a data base for statistical comparison of the various methods with emphasis on the multicomponent samplers under consideration for use in a national dry deposition network. The TDLAS was not available for a sufficient period of time to permit the collection of enough weekly samples to simulate network operation adequately on a statistical basis. As a result, daily sampling periods were planned.

The study was conducted at the EPA dry deposition station in Research Triangle Park, NC between 29 September and 12 October, 1986. Daily averaging and/or sampling times were employed for the 13-day study; weekly samples were also collected, but results from these samples are not compared in this report. Ambient concentrations of the following constituents are compared: total particulate and gaseous nitrate, nitric acid, nitrogen dioxide, total particulate sulfate, and total particulate ammonium.

Comparison of the results permits the following conclusions to be drawn:

- Total NO_3^- as measured by the ADS, TFR, and FP are in good agreement (i.e., differences between the results of the FP and either the ADS or TFR are not significant at the 95 percent confidence level).
- Total SO_4^{2-} as measured by the ADS, TFR, and FP are in good agreement (i.e., differences between the results of the FP and either the ADS or TFR are not significant).

- Nitrogen dioxide as measured by the TFR and TDLAS are highly correlated, although differences between the two sets of results are statistically significant. Nitrogen dioxide concentrations as measured by the LMA-3s and PSDs are more variable. Differences between the results of the TDLAS and those of one of the two LMA-3s are significant, as are the differences of TDLAS results and those of one of the two sets of PSDs.

- Nitric acid as measured by the ADS, FP, and TFR (FP), a nonstandard interpretation of TFR data, are in good agreement with those of the TDLAS (i.e., the differences between the TDLAS results and those of each of the three listed measures are not significant at the 95 percent confidence level). Two sets of TFR results were collected by independent operators (RTI and EPA). Differences between TDLAS results and one of the TFR results are significant. The daily TFR results are consistently much higher than those of the TDLAS. The five daily TFR(EPA) measures of HNO_3 are also consistently higher but are in better agreement with TDLAS results.

- Particulate ammonium as measured by the TFR and FP are in good agreement (i.e., differences between the two sets of results are not significant). Significant differences were found for the ADS and FP results with the FP results exceeding those of the ADS.

SECTION 3
EXPERIMENTAL

This study was conducted at the site of the EPA dry deposition network station at the edge of a parking lot serving the Environmental Research Center Annex, Reseach Triangle Park, NC. The sampling schedule is shown in Table G-2. The placement of the Unisearch van and the AES van, with respect to the station, is shown in Figure G-1. Duplicate daily TFR, ADS, and FP samplers, as well as weekly ADS and TFR samplers, were placed on the roof of the station. Triplicate PSDs were located on the roof also, while a second set of triplicate PSDs was placed inside the station and exposed to ambient air brought into the station through a large diameter manifold. Two Scintrex Model LMA-3 Luminox NO_2 monitors and the TDLAS were located inside the Unisearch van. Inlets for these units were positioned adjacent to the station near the TFR and ADS inlets. Short- term filter pack sampling units were located on the roof of the AES van. Figures G-2 and G-3 depict the sampling equipment and its location on the roof of the station.

The study plan relied on weekly TFR results from the EMSL-operated EPA network station. These data are not available for inclusion in the current report. Quality control checks indicate TFR(EPA) results for HNO_3 and Fine NO_3^- to be suspect for one of the two weekly ASRL-operated TFR samples. Results from weekly samples are not compared in this report.

The TFR and ADS systems are described in the text of the RTI final report (5). The FP is an open-face triple filter pack designed by the AES. The three filters are: first, a 2 µm pore size Teflon filter (with Teflon support mat, Gelman Corp.) for trapping atmospheric particles; second, a 1 µm pore size nylon filter (Gelman Corp.) for collecting nitric acid, and last, a Whatman 41 filter, impregnated with an aqueous solution of 10 percent v/v glycerol and 25 percent w/v potassium carbonate (K_2CO_3), for collecting gaseous sulfur dioxide. Duplicate filter packs were run for the daily samples using pumping stations that incorporated electronic mass flow meters. Flow rates were checked before and after each run using a dry gas meter.

TABLE G-2. SAMPLING SCHEDULE

	September		October										
	29	30	1	2	3	4	5	6	7	8	9	10	11
TFR (daily)	x	x	x	x	x	x	x	x	x	x	x	x	x
ADS (daily)	x	x	x	x	x	x	x	x	x	x	x	x	x
FP (daily)	x	x	x	x	x	x	x	x	x	x	x	x	x
LMA-3 (continuous)	--												
PSDs (daily)	x	x	x	x	x	x	x	x	x	x	x	x	x
TDLAS (continuous)	--												
TFR (weekly)	--												
ADS (weekly)	--												
FP (weekly)	--												
PSDs (weekly)	--												

Note:

a. Study: begins 1030 9/29/86; continues for 13 days; ends 0830 10/12/86.
b. Daily Schedule: 0830 to 1030 - sample changeover, equipment calibration and maintenance;
1030 to 0830 (next day) - sampling
c. Weekly Schedule: week 1 sampling 9/30/86 to 10/07/86;
week 2 sampling 10/07/86 to 10/13/86 (short week due to power shutoff)

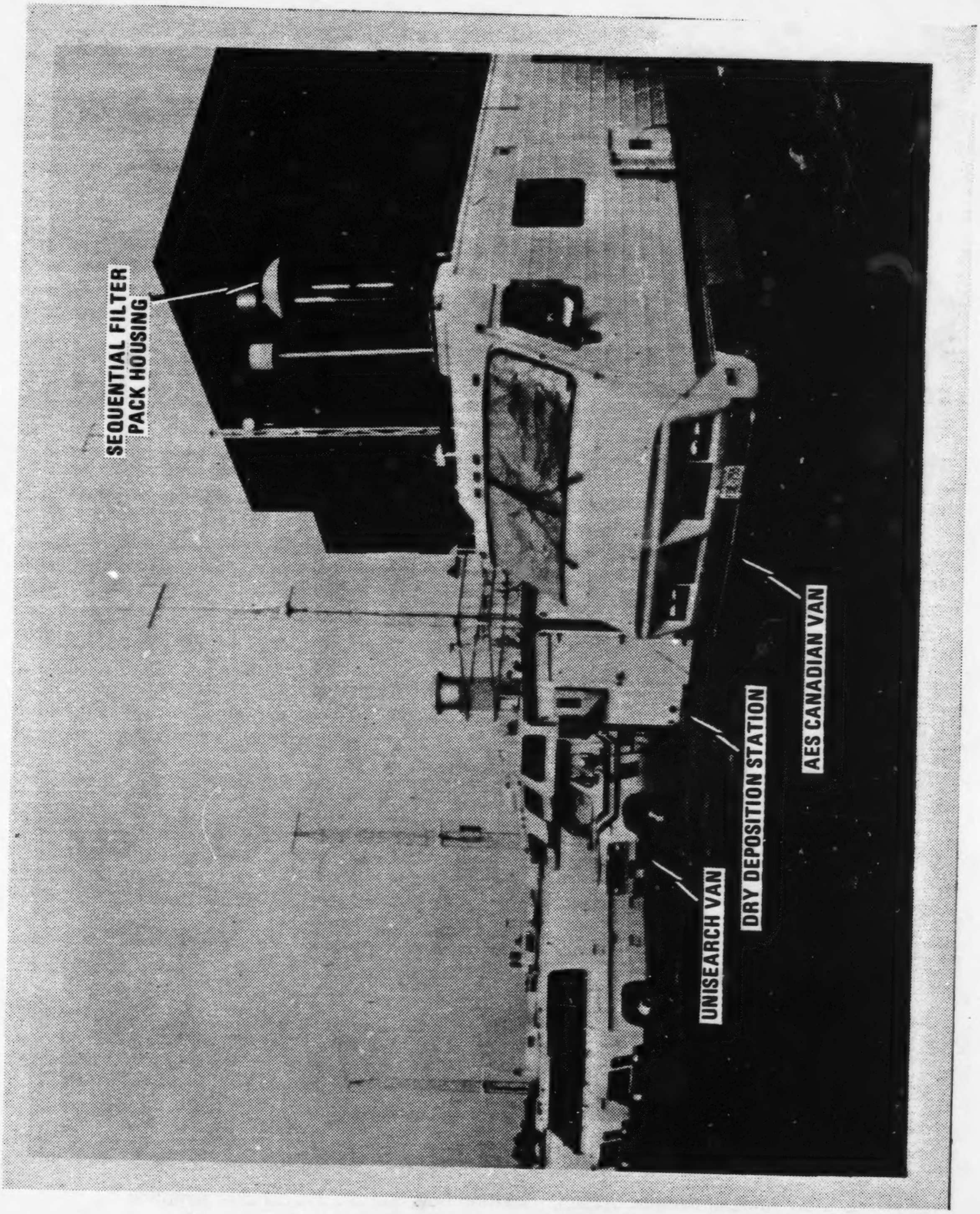

SEQUENTIAL FILTER PACK HOUSING
UNISEARCH VAN
DRY DEPOSITION STATION
AES CANADIAN VAN

Figure G-1. Location of sampling stations for the study.

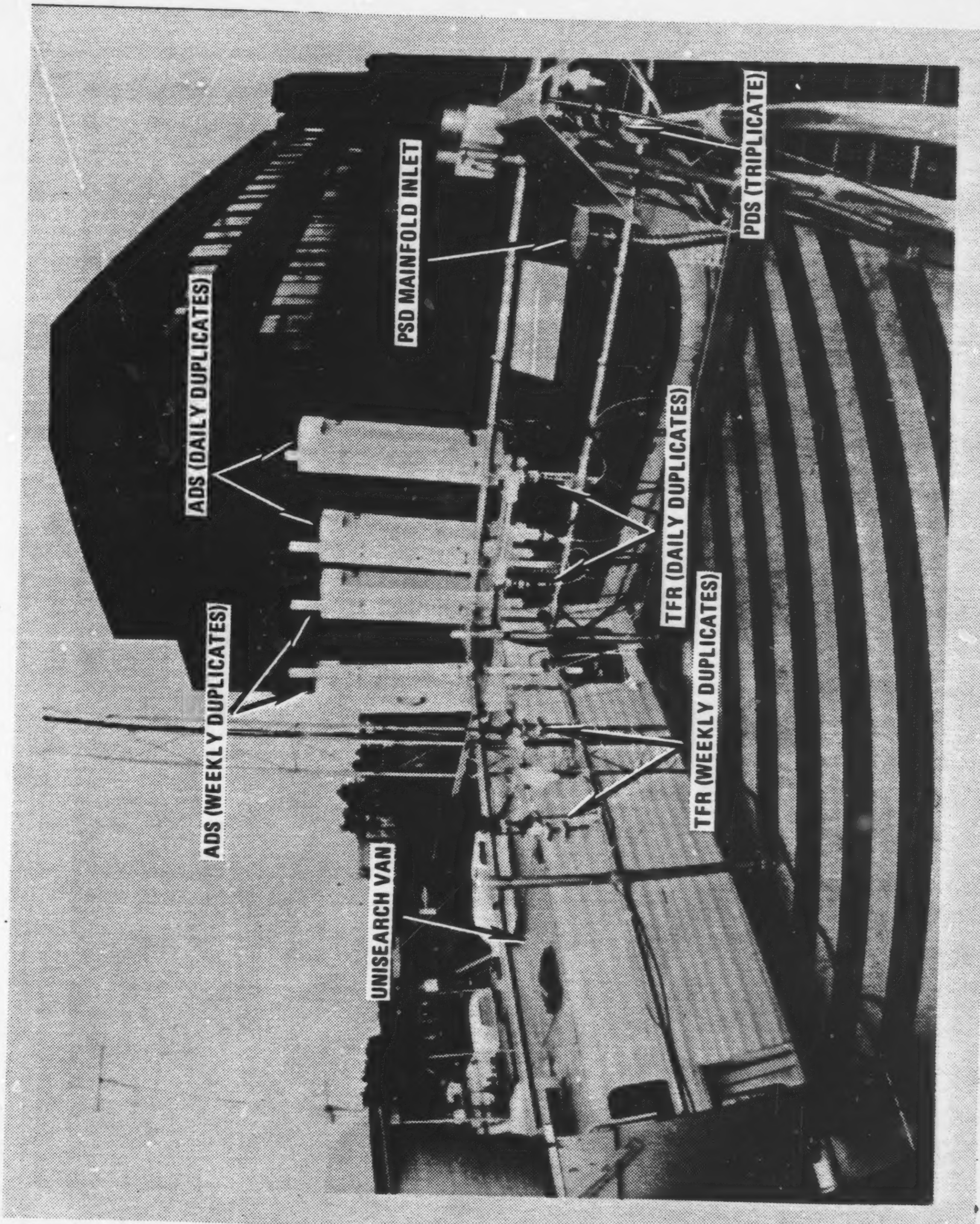

ADS (DAILY DUPLICATES)
PSD MAINFOLD INLET
PDS (TRIPLICATE)
TFR (DAILY DUPLICATES)
TFR (WEEKLY DUPLICATES)
ADS (WEEKLY DUPLICATES)
UNISEARCH VAN

Figure G-2. Annular denuder system, transition flow reactor, and personal sampling device placement on dry deposition station.

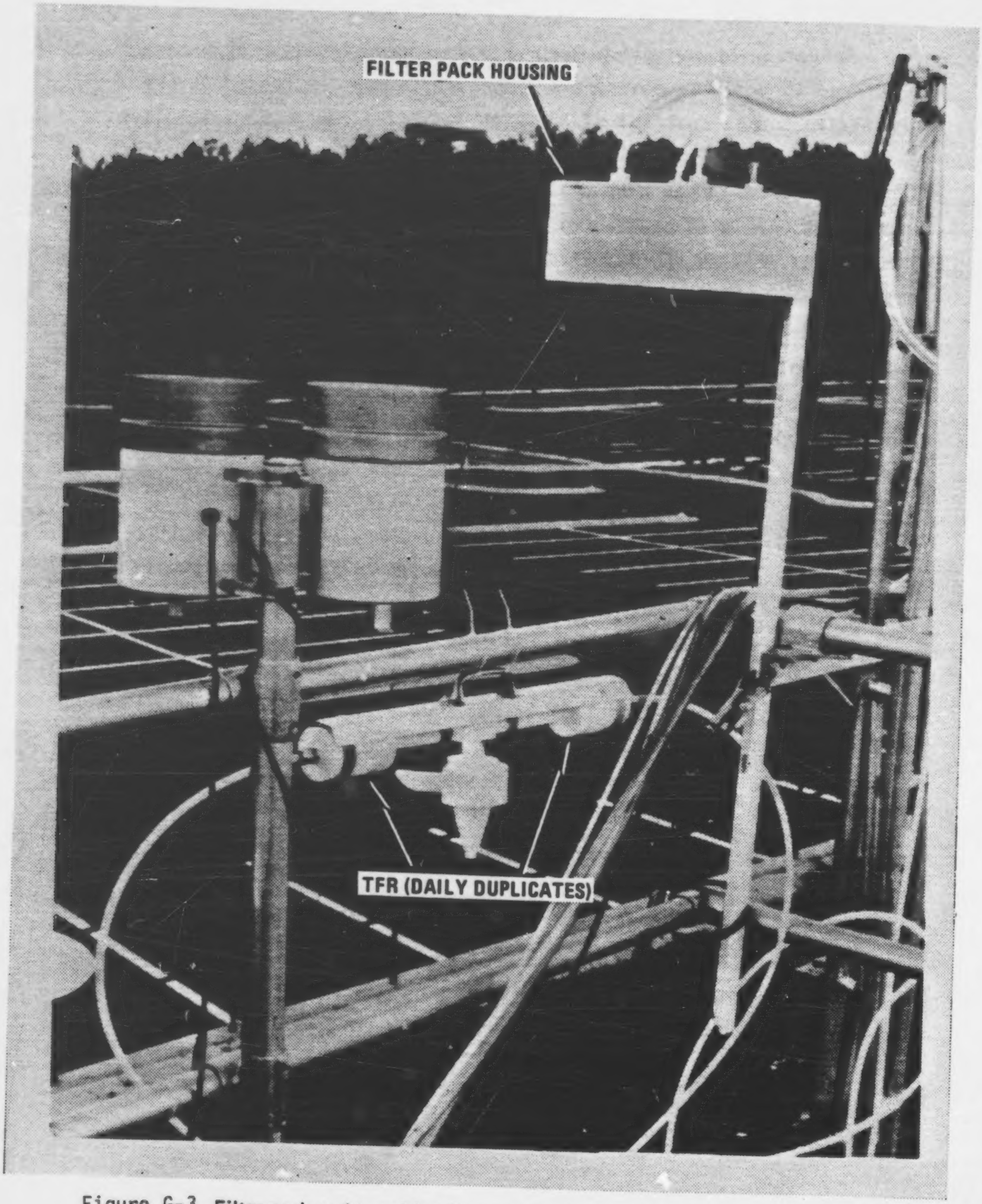

FILTER PACK HOUSING
TFR (DAILY DUPLICATES)

Figure G-3. Filter pack and transition flow reactor (second daily sample) placement on dry deposition station

Operation of the LMA-3 Luminox NO_2 monitors has been described elsewhere (6). These monitors are continuous monitors based on the chemiluminescence reaction of NO_2 with luminol in an aqueous solution. The formulation of the solution influences the extent of interferences from other oxidants such as ozone, peroxyacetylnitrate and sulfur dioxide and can also change the sensitivity and range of linearity in response as well as the effective lifetime of the solution. The solutions used in the study were batch No. 86083 prepared by Scintrex of Canada. Details, including discussion of the calibration procedure, quality control procedures, and data acquisition procedures, are available in draft form from Northrop Services (see paper 6, Table G-1). The TDLAS was operated by Dr. G. I. Mackay of Unisearch Associates, one of the designers of the TDLAS. The system is used to estimate trace gas concentrations by monitoring the position and extent of infrared absorption by the target molecular species (7). Specialized multipass optics and low pressure spectral scans inside an enclosed multipass cell permit the sensitive detection of NO_2 and HNO_3.

The PSDs for NO_2 were adapted from a design in current use for volatile organic compounds (8). The adsorbent for the volatile organics was replaced by a triethanolamine-coated cellulose filter for sorption of NO_2. The PSDs were exposed outside in the ambient air under variable wind conditions as well as inside the dry deposition station where they were exposed inside a manifold leading from the outside. Ambient air was passed through the manifold at a controlled linear velocity of 1.0 m s^{-1}.

A summary of the results to be compared for each of the methods is given in Table G-3.

TABLE G-3. RESULTS TO BE COMPARED

Species	ADS	TFR	FP	TDLAS	LMA-3	PSD
Total NO_3^-	x	x	x			
HNO_3	x	x,x[a]x[b]	x[c]	x		
NO_2		x		x	x	x
Total NH_4^+	x,x[d]	x,x[d]	x			
Total SO_4^{2-}	x	x	x			

[a] HNO_3 computed from TFR results assuming it operates similarly to an FP; it considers the sum of NO_3^- recovered from the nylon strip and filter and is designated TFR (FP).

[b] HNO_3 was independently measured by Tom Ellestad of the Atmospheric Sciences Research Laboratory (ASRL) of the U.S. EPA using equipment that was nominally identical to the equipment used by RTI (supplied to RTI by Ellestad).

[c] HNO_3 from the FP assumes no particle NO_3^- volatilization and that the NO_3^- on the nylon filter represents only HNO_3.

[d] Total gaseous and particulate ammonia and ammonium (Total NH_3+NH_4^+) are also considered.

SECTION 4

RESULTS AND DISCUSSION

Studywide species profiles of daily means are shown in Figures G-4 to G-10. The performance of each method can be evaluated by comparing the results summarized in Table G-4. Studywide averages for each measure are listed in Table G-4. Table G-4 also presents correlation coefficients and average ratios of daily mean measurements that compare results from the ADS, TFR, and FP with those of either the FP or TDLAS. Mean differences between daily measurement results and those of either the FP or TDLAS were evaluated using t tests to evaluate their significance at the 95 percent confidence level. Results of these tests are also given in Table G-4.

Since different amounts of particulate matter were expected to be collected in the cyclone inlets of the ADS and the TFR, the cyclones were extracted following each daily run, and the extract was analyzed for NO_3^-, NH_4^+, and SO_4^{2-}. These values were added to the quantities found elsewhere in the sampling systems. In the following discussion, Total NO_3^- refers to the sum of gaseous and particulate nitrate, Total NH_4^+ and Total SO_4^{2-} refer to total particulate NH_4^+ and total particulate SO_4^{2-}, respectively. All concentration readings are referenced to 0° C and 760 mm.

Total NO_3^---

As indicated by the profiles in Figure G-4 and the average concentrations in Table G-4, the Total NO_3^- as determined by the ADS, TFR, and FP are in good agreement. The ADS and FP measures are well correlated (i.e., $r = 0.88$) and show an average daily ratio of 1.029 ± 0.104. The corresponding TFR and FP measures are highly correlated (i.e., $r = 0.94$) with an average daily ratio of 1.036 ± 0.094. The average daily range for the three samplers is 0.356 ± 0.109 $\mu g/m^3$. Significant differences were not found when the FP Total NO_3^- was compared with the ADS or with the TFR measures of Total NO_3^-.

TABLE G-4. COMPARISON OF RESULTS

Measure	Mean ± SD($\mu g/m^3$)	Correlation Coefficient	Average Ratio	t Test Results
Total NO_3^- ADS	3.086 ± 0.586	0.88	1.029 ± 0.104	no difference
Total NO_3^- TFR	3.141 ± 0.739	0.94	1.036 ± 0.094	no difference
Total NO_3^- FP*	3.016 ± 0.589	--	--	--
HNO_3 ADS	1.509 ± 0.627	0.81	0.948 ± 0.256	no difference
HNO_3 TFR	2.715 ± 0.847	0.81	1.762 ± 0.351	TFR > TDLAS
HNO_3 TFR (EPA)**	1.998 ± 0.700	0.87	1.360 ± 0.212	--
HNO_3 TFR (FP)	1.712 ± 0.644	0.84	1.080 ± 0.258	no difference
HNO_3 FP	1.715 ± 0.668	0.87	1.078 ± 0.250	no difference
HNO_3 TDLAS*	1.564 ± 0.505	--	--	--
NO_2 TFR	19.172 ± 6.935	0.97	1.069 ± 0.089	TFR > TDLAS
NO_2 LMA-3 (1)	18.399 ± 5.749	0.94	1.007 ± 0.111	no difference
NO_2 LMA-3 (2)	20.972 ± 7.029	0.91	1.191 ± 0.171	LMA-3(2)>TDLAS
NO_2 PSD (i)	20.342 ± 4.953	0.86	1.184 ± 0.208	PSD(i)>TDLAS
NO_2 PSD (o)	18.119 ± 4.741	0.47	1.076 ± 0.323	no difference
NO_2 TDLAS*	17.923 ± 6.062	--	--	--
Total NH_4^+ ADS	1.827 ± 1.063	0.96	0.777 ± 0.159	ADS < FP
Total NH_4^+ TFR	2.279 ± 1.092	0.92	1.036 ± 0.227	no difference
Total NH_3+NH_4^+ ADS	2.545 ± 1.153	0.94	1.171 ± 0.262	no difference
Total NH_3+NH_4^+ TFR	2.911 ± 1.191	0.88	1.391 ± 0.374	TFR > FP
Total NH_4^+ FP*	2.391 ± 1.444	--	--	--
Total SO_4^{2-} ADS	6.687 ± 3.332	0.98	0.984 ± 0.099	no difference
Total SO_4^{2-} TFR	6.528 ± 3.238	0.97	0.961 ± 0.100	no difference
Total SO_4^{2-} FP*	6.907 ± 3.773	--	--	--

*The designated measure against which the previous measures within each grouping is compared to arrive at correlation coefficients, average ratios, and the t test results (at the 95 percent confidence level).

**The number of paired samples in most cases is 13; however, in this case, it is 5.

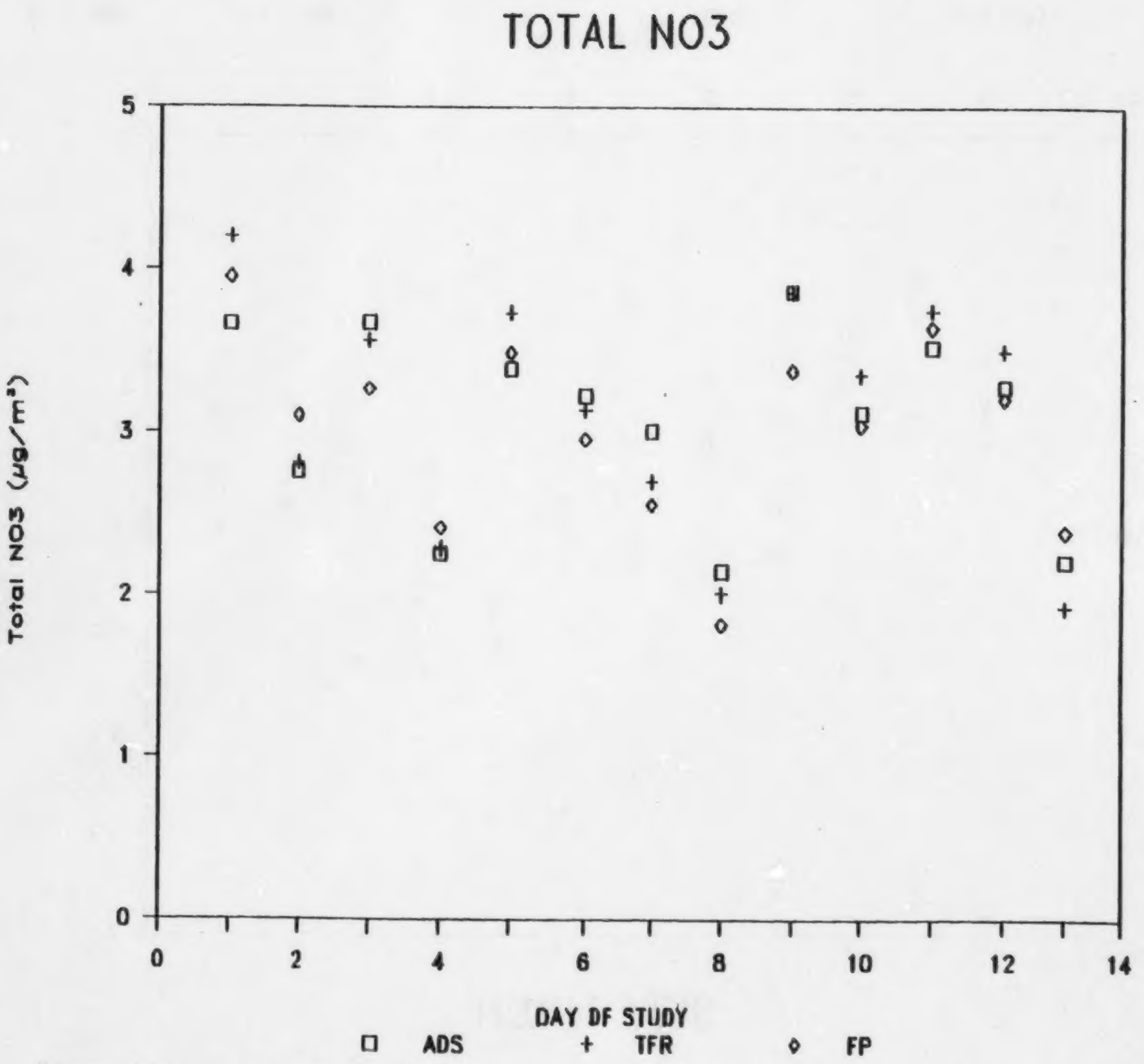


Figure G-4. Mean daily Total NO_3^- concentrations from ADS, TFR, and FP samplers.

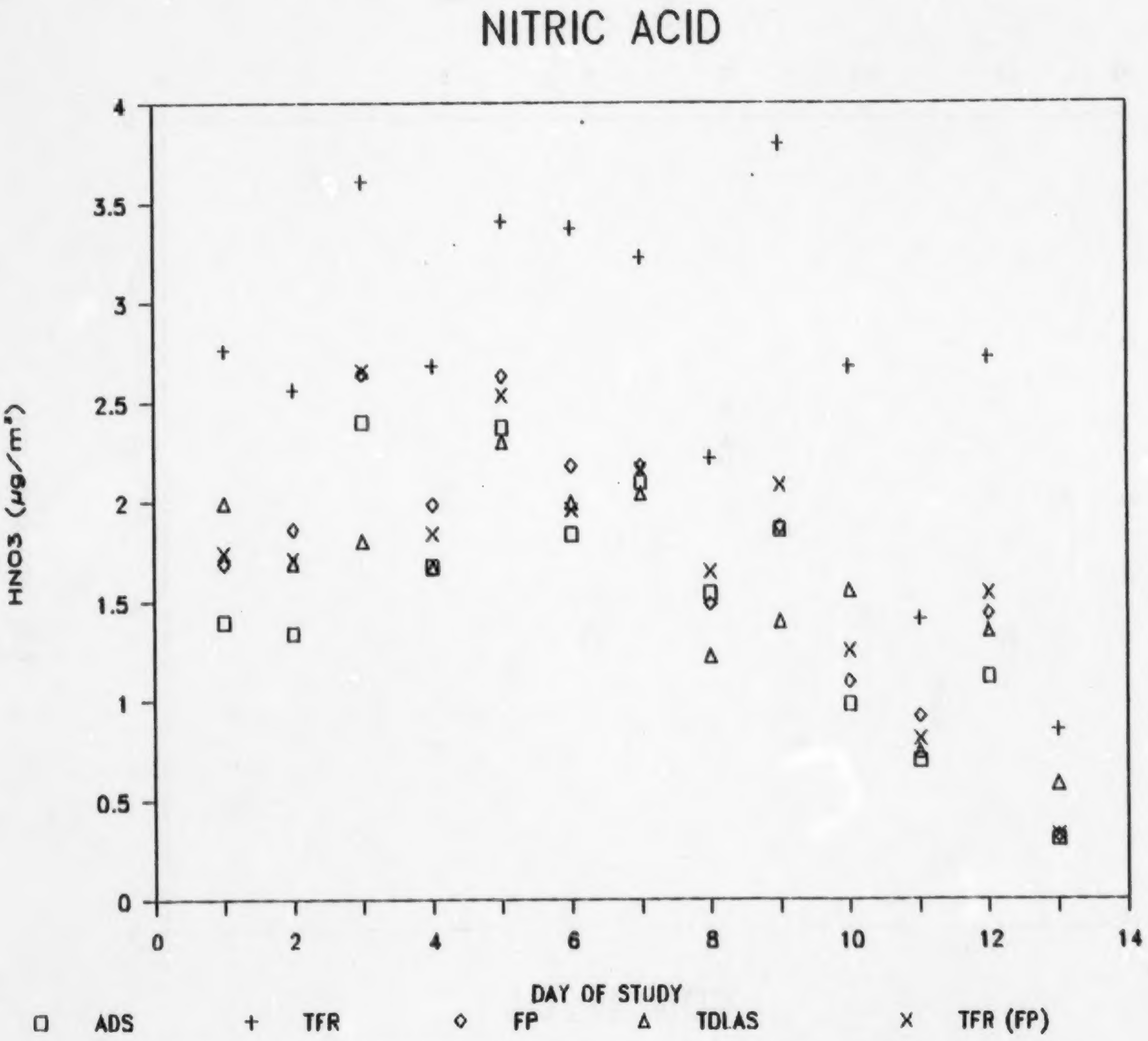


Figure G-5. Mean daily HNO_3 concentrations from ADS, TFR, TFR(FP), FP, and TDLAS techniques.

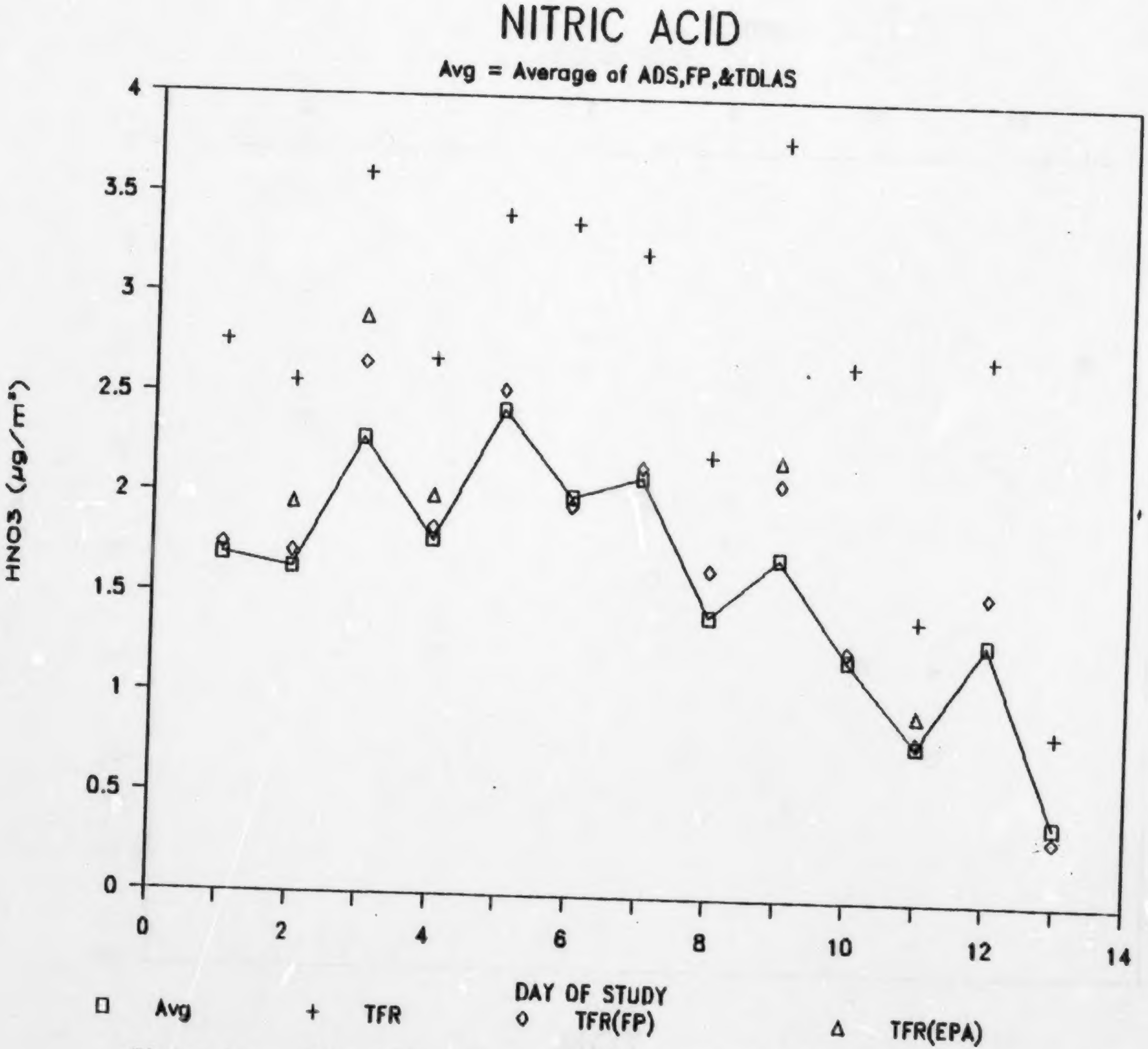


Figure G-6. Mean daily HNO_3 concentrations from TFR, TFR(FP), TFR(EPA), and consensus of ADS, FP, and TDLAS techniques.

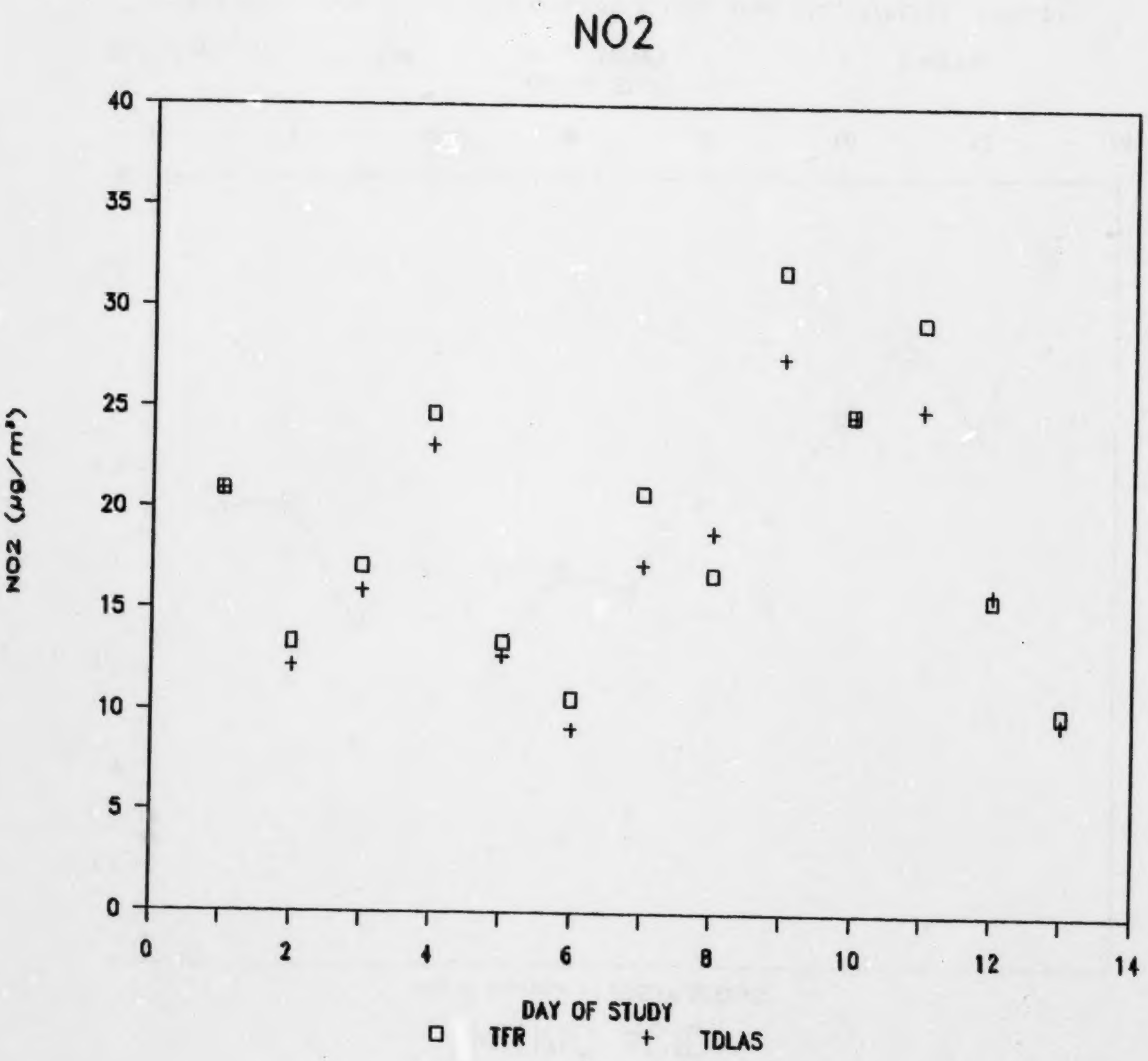


Figure G-7. Mean daily NO_2 concentrations from TFR and TDLAS techniques.

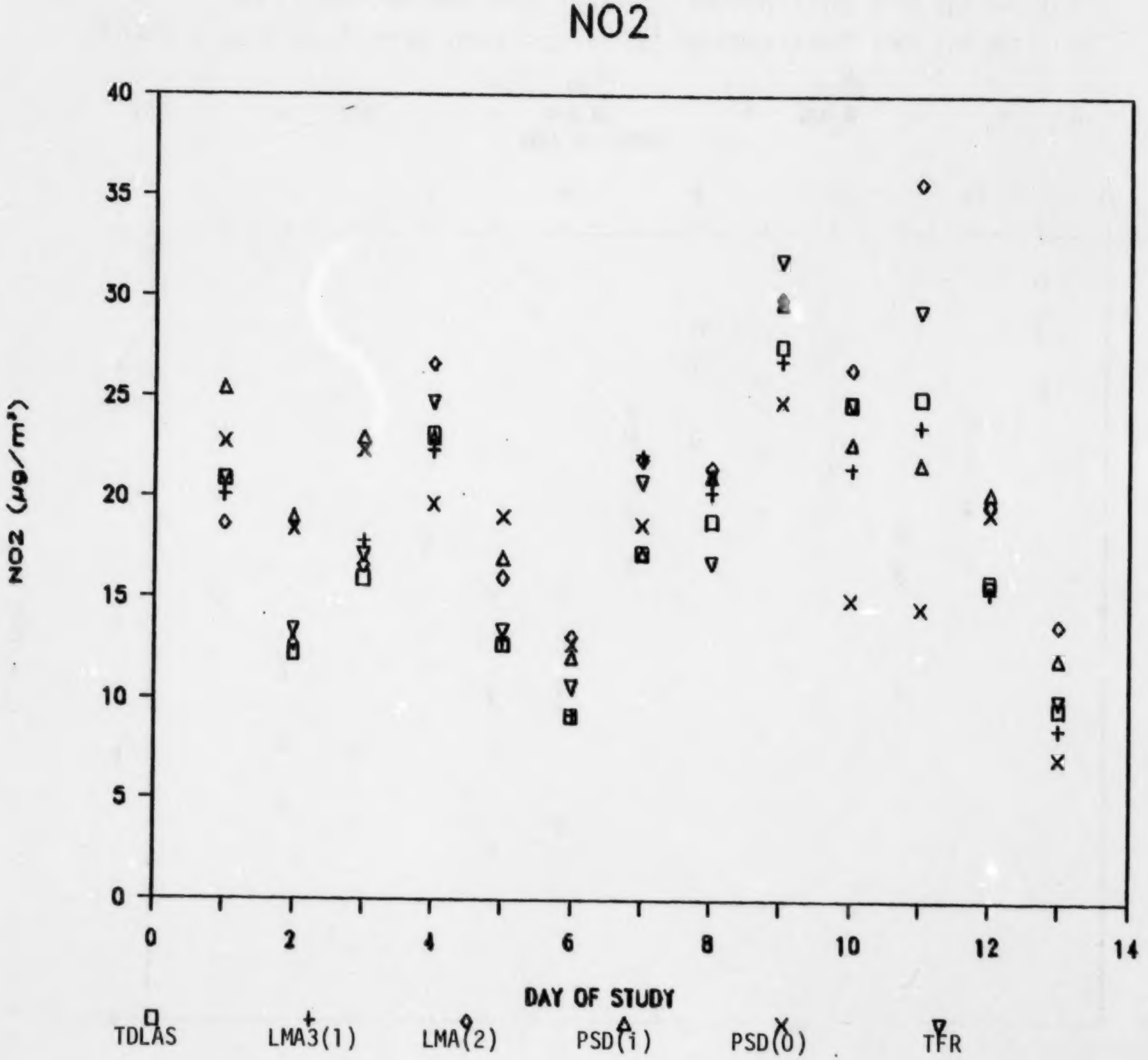


Figure G-8. Mean daily NO_2 concentrations from TDLAS, LMA-3 (1), LMA-3 (2), PSD (i), PSD (o), and TFR techniques.

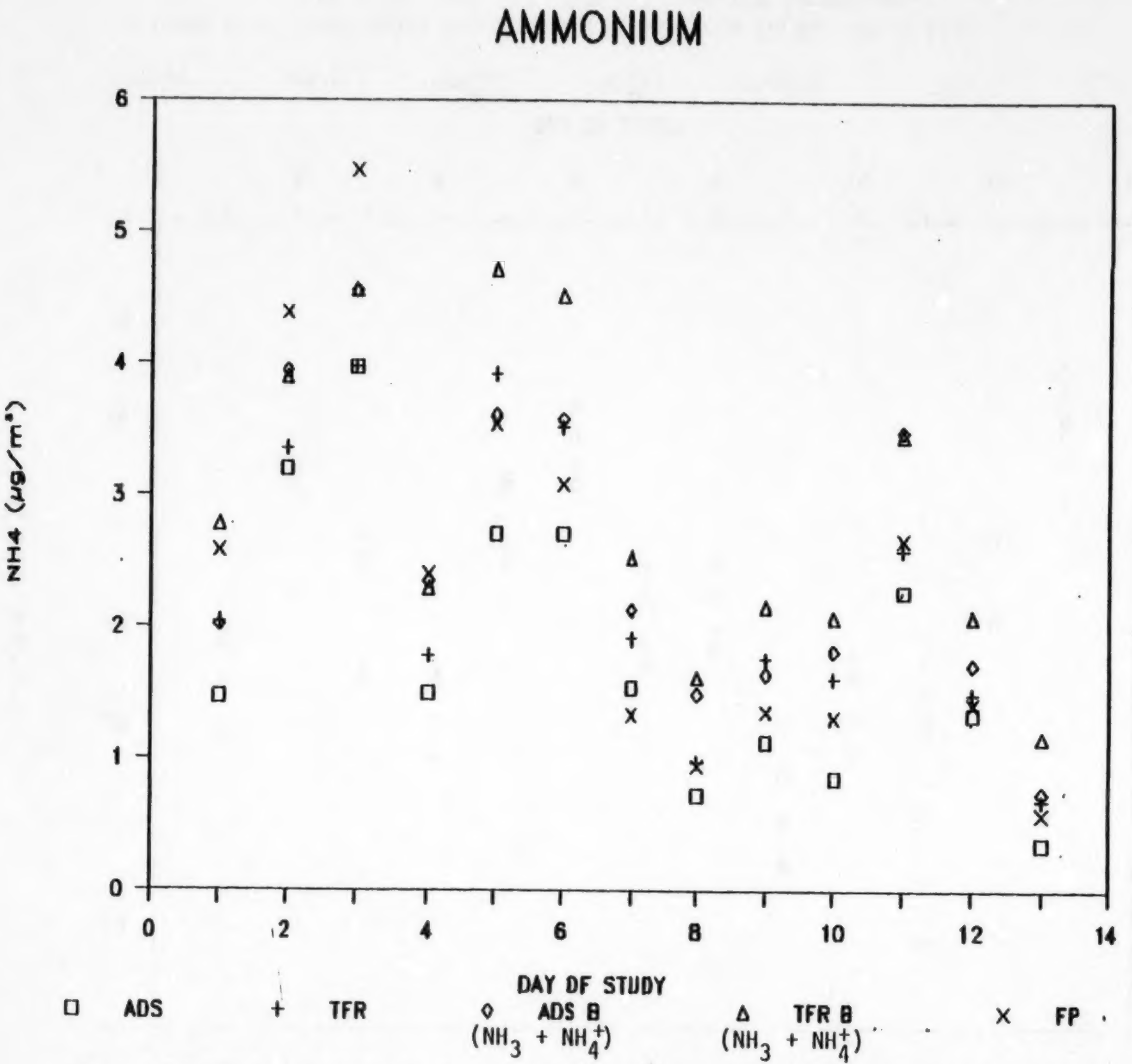


Figure G-9. Mean daily Total (particulate) NH_4^+ concentrations from the ADS, TFR, and FP samplers and Total (NH_3+NH_4^+) concentration from ADS and TFR samplers.

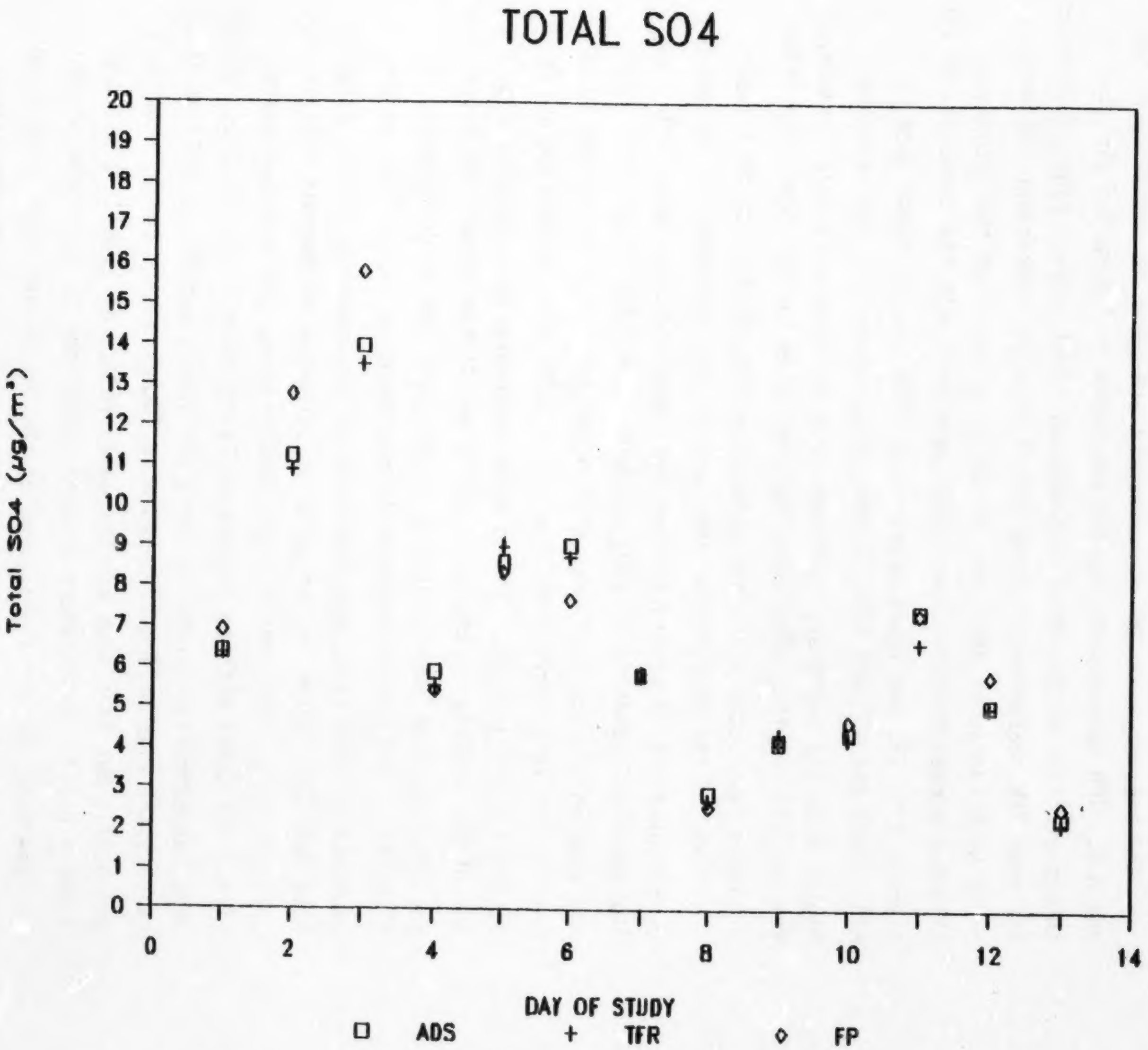


Figure G-10. Mean daily Total (particulate) SO_4^{2-} concentrations from ADS, TFR, and FP samplers.

HNO3--

Thirteen days of HNO_3 measurements are shown in both Figures G-5 and G-6. TFR measurements by RTI are shown in Figure G-5 with two interpretations of the resulting data as noted below. Figure G-6 shows the same TFR measurements along with 5 days of independent TFR measurements by Ellestad of ASRL, one of the originators of the technique. Ellestad's measurements show better agreement with the consensus of the average ADS, FP, and TDLAS measures of HNO_3 than do those made by RTI. Both the RTI and EPA TFR HNO_3 measurements are consistently higher than the consensus, although this difference is more pronounced for the RTI results. The cause for this bias has not been identified, although laboratory tests are planned by EMSL to address this issue.

Four of the measures of HNO_3 are in good agreement as indicated by the profiles in Figure G-5 and the comparisons in Table G-4. The ADS and TDLAS measures of HNO_3 are well correlated (i.e., $r = 0.81$) and show an average daily ratio of 0.948 ± 0.256. The FP and TDLAS results are well correlated (i.e., $r = 0.87$) with an average daily ratio of 1.078 ± 0.250. Nitric acid concentrations computed from the sum of the nitrate on the nylon strip and filter of the TFR assume that the TFR functions similarly to a filter pack and is designated "TFR(FP)." TFR(FP) is expected to represent an upper limit on the estimate of HNO_3 since any fine particulate ammonium nitrate volatilized from the Teflon filter would be collected as gaseous HNO_3 on the nylon filter. The TFR(FP) and TDLAS results are well correlated (i.e., $r = 0.84$) with an average daily ratio of 1.080 ± 0.258. Nitric acid concentrations computed using TFR theory and RTI as well as EPA results are also well correlated with TDLAS results (i.e., r of 0.81 and 0.87), but they show average daily ratios of 1.762 ± 0.351 and 1.360 ± 0.212. Differences between TDLAS results and those of the RTI-operated TFR are significant at the 95 percent confidence level. Too few TFR (EPA) data are available to permit a fair comparison. Significant differences were not found when the TDLAS HNO_3 results were compared with the corresponding results of the ADS, FP, or TFR(FP).

NO_2--

As shown by the profiles in Figure G-7 and by the average concentrations in Table G-4, the NO_2 concentration as determined by the TFR and TDLAS are in good agreement. The two measures are highly correlated (i.e., $r = 0.97$) with an average daily ratio of 1.069 ± 0.089. The average daily range and difference for the two measures is 1.337 ± 1.721 $\mu g/m^3$ and 0.494 ± 2.152 $\mu g/m^3$. Differences between these two measures of NO_2 are significant.

The comparisons between the TDLAS and the other measures of NO_2 are illustrated in Figure G-8. Average daily values from each of the two LMA-3 Luminox instruments and from each of the two daily sets of triplicate PSDs are displayed. Both sets of LMA-3 NO_2 measures are well correlated with the TDLAS results (i.e., r values of 0.94 and 0.91). They show average daily LMA-3 to TDLAS ratios of 1.007 ± 0.111 and 1.191 ± 0.171. Comparison of LMA-3(1) and TDLAS results do not show differences significant at the 95 percent confidence level. In contrast, differences between the LMA-3(2) and TDLAS results and also between the results of the two LMA-3 analyzers are significant.

The results of the PSDs(i) are well correlated with those of the TDLAS (i.e., $r = 0.86$) with an average daily ratio of 1.184 ± 0.208. Comparison of the PSD(i) and TDLAS results show differences significant at the 95 percent confidence level. Although the correlation coefficient is low (i.e., $r = 0.47$), the average ratio is near unity (i.e., 1.076 ± 0.323) for the PSD(o) and the TDLAS results. The larger variability of the comparison between the PSD(o) and TDLAS results does not permit the detection of a significant difference between the two. Comparison of the results of the two sets of PSDs shows differences significant at the 90 percent confidence level but not at the 95 percent level.

Total NH_4^+--

Previous analyses (5) have suggested that lost, volatilized ammonium in the ADS may cause a low bias of Total NH_4^+ in this sampler.

The FP is likely to experience an ammonia sampling artifact that would occur if ammonia were captured by cocollected acidic species on the Teflon filter. These points suggest that the TFR Total NH_3 + NH_4^+ should exceed the FP Total NH_4^+, and that the FP Total NH_4^+ should exceed the ADS Total NH_4^+.

Five ammonium-related parameters follow similar trends as indicated in Figure G-9. The average concentrations displayed in Table G-4 show fair agreement, and the previously described anticipated comparisons are confirmed. The TFR and FP Total NH_4^+ are highly correlated (i.e., $r = 0.92$) and show an average daily ratio of 1.036 ± 0.227. The ADS Total NH_3+ NH_4^+ and FP Total NH_4^+ are also highly correlated (i.e., $r = 0.94$) with an average daily ratio of 1.171 ± 0.262. The TFR NH_3+ NH_4^+ results are highly correlated with those of the FP (i.e., $r = 0.88$). The TFR results exceed those of the FP as indicated by the average daily ratio (i.e., 1.391 ± 0.374). The ADS and FP Total NH_4^+ are highly correlated (i.e., $r = 0.96$). The average daily ratio of 0.777 ± 0.159 shows that the Total NH_4^+ results from the ADS are less than those from the FP.

Significant differences were found from comparisons of FP Total NH_4^+ with the TFR NH_3 + NH_4^+ and also with the ADS Total NH_4^+. Significant differences were not found when the FP Total NH_4^+ was compared with TFR Total NH_4^+ or with the ADS NH_3+NH_4^+.

Total SO_4^{2-}--

ADS, TFR, and FP measures of Total SO_4^{2-} are in excellent agreement as indicated by the profiles in Figure G-10 and the average concentrations in Table G-4. The ADS and FP measures are highly correlated (i.e., $r = 0.98$) with an average daily ratio of 0.984 ± 0.099. The corresponding TFR and FP measures are highly correlated (i.e., $r = 0.97$) and show an average daily ratio of 0.961 ± 0.100. The average daily range for the three samplers is 0.779 ± 0.664 "g/m^3. Significant differences were not found when the FP Total SO_4^{2-} was compared with the ADS or with the TFR measures of Total SO_4^{2-}.

REFERENCES

1. Anlauf, K. G., Fellin, P., Wiebe, H. A., Schiff, H. I., Mackay, G. I., Braman, R. S., and Gilbert, R. (1985). A Comparison of Three Methods for Measurement of Atmospheric Nitric Acid and Aerosol Nitrate and Ammonium. Atmos. Environ. 19: 325-333.

2. Knapp, K. T., Durham, J. L., and Ellestad, T. G. (1986). Pollutant Sampler for Measurements of Atmospheric Dry Deposition. Environ. Sci. and Technol. 20: 633-637.

3. Durham, J. L., Ellestad, T. G., Stockburger, L., Knapp, K. T., and Spiller, L. L. (1986). A Transition-Flow Reactor Tube for Measuring Trace Gas Concentrations. J. Air Pollut. Control Ass. 36: 1228-1232.

4. Possanzini M., Febo, A., and Liberti, A. (1983). New Design of a High Performance Denuder for the Sampling of Atmospheric Pollutants. Atmos. Environ. 17: 2605-2610.

5. Sickles, J.E., II, Main text of this document.

6. Schiff, H. I., Mackay, G. I., Castledine, C., Harris, G. W., and Tran, Q. (1986). A Sensitive Direct Measurement NO_2 Instrument. In Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants. EPA Report No. 600/9-86-013, pp. 834-844.

7. Schiff, H. I., Hastie, D. R., Mackay, G. I., Iguchi, T., and Ridley, B. A. (1983). Tunable Diode Laser Systems for Measuring Trace Gases in Tropospheric Air. Environ. Sci. and Technol. 17: 352A-364A.

8. Mulik, J. D. and Williams, D. (1986). Passive Sampling Devices for NO_2. In Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants. EPA Report No. 600/9-86-013, pp. 61-70.